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CANDIDATE SAMPLING AND ANALYSIS METHODS FOR 21 SUSPECT CARCINOGENS IN COMBUSTION EMISSIONS

by

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The report identifies candidate sampling and analysis methods for 21 suspect carcinogens in conventional coal and fuel oil combustion emissions. The methods were selected from an extensive review of existing techniques used to determine the substances in air and other matrices. In addition to identifying specific methods for each suspect carcinogen, the report describes a comprehensive sampling and analysis protocol which can be used to determine 13 of the suspect carcinogens. Costs for the separate candidate methods and for the comprehensive protocol are also provided.

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ABSTRACT

The purpose of this study was to identify candidate sampling and analysis techniques for twenty-one suspect carcinogens in conventional coal and fuel oil combustion sources. The research reported represents a collaboration of independent efforts conducted by Battelle's Columbus Laboratories and Arthur D. Little, Inc.

An initial effort was conducted to determine the probability that members of the listed carcinogens exist in combustion emissions. Eight of the substances—arsenic, beryllium, cadmium, nickel, polynuclear aromatic hydrocarbons (PAH), 2,3,7,8-tetrachlorodibenzodioxin (dioxin), formaldehyde, and trichloroethylene—have been reported in combustion sources. The potential of the remaining carcinogens for formation in combustion emissions was determined based on an evaluation of thermodynamic potentials, possible synthesis reactions, and combustion formation conditions. Asbestos and benzene were assessed as having a reasonable probability of being found in stack gases from coal and fuel oil combustion. Three compounds—acrylonitrile, vinyl chloride, and vinylidene chloride—were identified as having a low probability of appearing in combustion discharges, while the remaining eight materials—perchloroethylene, ethylene dichloride, ethylene dibromide, ethylene oxide, diethylnitrosamine, dimethylnitrosamine, N-nitroso-N-ethylurea, and N-nitroso-N-methylurea—were listed as having an even lower (minimal) probability of appearing in discharges.

Existing sampling and analysis methodology for the twenty-one suspect carcinogens were reviewed to provide a basis for selecting candidate procedures for these compounds in combustion emissions. For the majority of the substances, methods have not been developed specifically for determination in this matrix. Based on general requirements for air sampling, the features of three major methods—Source Assessment Sampling System (SASS) train, EPA Method 5 train, and grab sampling—were compared for emission applications. For analysis, EPA, IERL/Research Triangle Park, Level 1 Environmental Assessment procedures, and EPA standard methods for the compounds were examined. Additional documented sampling and analysis methods were also reviewed for each suspect carcinogen.

From the information obtained in the review of existing methodology, specific sampling and analysis procedures were recommended for each compound. Sampling recommendations primarily involved variations of SASS train, Method 5 train, and grab sampling methods. Separate procedures were identified for arsenic and formaldehyde. Several sampling methods were suggested for asbestos since the reliability of any one method has yet to be proven. For analysis of the organic compounds, gas chromatography, mass spectrometry, and high performance liquid chromatography methods were included in the recommendations. Atomic absorption spectroscopy was suggested for the inorganic elements. For asbestos, analysis with transmission electron microscopy was identified.

In an adjunct effort, a combined approach to sampling and analysis was examined based on the redundancies in the recommended methods. Combined procedures were incorporated into a protocol for a comprehensive field program to determine thirteen of the suspect carcinogens in combustion emissions. A detailed cost model estimating equipment expenses, personnel costs, planning and reporting expenses, and other factors was developed for the comprehensive field program. Sampling and analysis costs were also estimated for each of the twenty-one suspect carcinogens based only on the per sample price and not on the cost of purchasing instrumentation or deploying sampling teams in the field.

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency has an ongoing commitment to identify and control toxic materials in the environment. Increased attention has recently focused on a group of compounds designated as suspect carcinogens. The twenty-one substances listed below are among this group:

acrylonitrile
arsenic
asbestos
benzene
beryllium
cadmium
diethylnitrosamine
dimethylnitrosamine
dioxin derivatives
ethylene dibromide
ethylene dichloride
ethylene oxide
formaldehyde
nickel
N-nitroso-N-ethyl urea
N-nitroso-N-methyl urea
perchloroethylene
polynuclear aromatic hydrocarbons (PAH)
trichloroethylene
vinyl chloride
vinylidene chloride

The possible formation and associated hazards of these compounds in conventional coal and fuel oil combustion are of special interest to the U.S. EPA. The presence of these species in combustion emissions must be evaluated before appropriate control measures can be initiated. Although sampling and analysis techniques have been developed and applied for the determination of the suspect carcinogens in a variety of matrices, few methods have been documented for their determination in combustion emissions. Valid techniques are therefore needed which can be used to characterize the occurrence of the suspect carcinogens in this matrix.

The work reported here represents a combination of independent studies conducted by Battelle's Columbus Laboratories and Arthur D. Little, Inc. The major objective of the research was to identify candidate methods for the qualitative and quantitative determination of the suspect carcinogens in combustion emissions. Five interrelated efforts were conducted in the two independent studies. These efforts are described in this report as follows:

(1) Evaluate the potential for emission of the suspect carcinogens from combustion processes.

(2) Review existing sampling and analysis methods for the compounds under study.

(3) Recommend procedures for determination of the suspect carcinogens in combustion emissions based on the review and utilizing EPA reference methods where available.

(4) Investigate the extent to which individual sampling and analysis techniques can be applied to two or more substances simultaneously and incorporate the multicomponent techniques into a comprehensive field study protocol.

(5) Provide a cost estimate for sampling and analyzing the suspect carcinogens in combustion emissions.

SECTION 2

CONCLUSIONS

Of the twenty-one suspect carcinogens considered, eight have been reported from conventional coal and fuel oil combustion sources. These eight substances include formaldehyde, trichloroethylene, 2,3,7,8-tetrachlorodibenzodioxin, PAH, arsenic, beryllium, cadmium, and nickel. The presence of acrylonitrile, asbestos, benzene, vinyl chloride, and vinylidene chloride is highly probable based on thermodynamic stability, organic synthesis chemistry, and combustion conditions. The remaining eight compounds have a low to minimal probability of being present in combustion emissions. These substances are diethylnitrosamine, dimethylnitrosamine, ethylene dibromide, ethylene dichloride, ethylene oxide, N-nitroso-N-methyl urea, N-nitroso-N-ethyl urea, and perchloroethylene.

In reviewing available EPA methods and other methods for the suspect carcinogens, many procedures were identified which had been developed for sampling and analyzing these materials in air, water, wastewater, soil, human tissue, and other matrices. Few procedures, however, have been developed specifically for use in stationary conventional combustion sources. In general, analytical procedures intended for the determination of the suspect carcinogens in other types of matrices are expected to be directly applicable to combustion source samples, provided that suitable sample collection and sample preparation procedures can be specified for the combustion source application. The standard sampling procedures intended for media such as water or soil would usually not be appropriate for source emissions. Conversely, sampling procedures that have been developed explicitly for collection of particulate and vapor phase emissions from stationary combustion sources can be expected to be applicable to the suspect carcinogens even though they were originally designed for other species or for general emissions sampling. In addition, procedures intended for sampling and analysis of the suspect carcinogens in ambient air may be applicable to combustion source atmospheric emission sampling with suitable modifications.

Selection of specific methodology for determination of the suspect carcinogens was based on the review provided in this report. Sampling recommendations primarily involved variations of source assessment sampling systems (SASS), EPA Method 5 train, and grab sampling methods. Separate procedures were recommended for arsenic and formaldehyde. Several sampling methods were suggested for asbestos since the reliability of any one method has yet to be proven. For analysis of the organic compounds, gas chromatography, mass spectrometry, and high performance liquid chromatography methods were included in the recommendations. Atomic absorption spectroscopy was suggested for the inorganic elements. For asbestos, analysis with transmission electron microscopy was identified. The specific sampling and analysis procedures listed as candidates have not, in most cases, been subjected to the necessary laboratory and field validation needed to demonstrate the applicability, precision, accuracy or detection limits achievable in the context of combustion source environmental assessment. Therefore, the recommendations in this report could not always be supported with documentation of performance, although the candidate methods do represent the known state-of-the-art for collection and analysis of these types of materials. The candidate methods should, however, provide reliable estimates of the concentrations of the suspect carcinogens in combustion source effluents when employed in an environmental assessment program with adequate quality control.

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Redundancies in the individual sampling and analysis procedures allow them to be combined to reduce the cost and time requirements for determining this group of suspect carcinogens in combustion emissions. For example, one SASS train would suffice for the collection of all filter/sorbent compounds, i.e., the ureas, PAH, and inorganics. Additional cost and time reductions can be realized by limiting sampling and analysis to only those compounds which have been reported or which have a reasonable probability of being present in combustion emissions. In this case, the presence and potential hazards of those substances with a low potential for formation in combustion processes are assumed to be negligible. Based on early 1981 dollars, the cost for sampling and analyzing thirteen suspect carcinogens in a single comprehensive field study is estimated to be $62,000.

SECTION 3

RECOMMENDATIONS

On reviewing the information in this report, the following additional research is recommended:

1. Field studies should be conducted to determine the presence or absence of the nonreported suspect carcinogens in combustion emissions.
2. A detailed validation study should be performed on the recommended sampling and analysis techniques as well as the combined field study protocols to determine the reliability and limitations of the methods.
3. Emphasis should be placed on developing more low-cost screening tests to quickly rank collected samples before expensive analytical procedures are performed.
4. A new Level 2 sampling train for trace combustion emissions should be developed. This development is important since the current stainless steel SASS train may cause an interferent in metals analyses. Also, a new Level 2 sampling train would assist EPA in evaluating fine particulate ($<25\mu$) and benzo(a)pyrene (BaP) emissions especially if the proposed air quality standards are promulgated.

4

SECTION 4

POTENTIAL COMBUSTION EMISSIONS

The purpose of this initial effort was to determine the potential presence of the twenty-one suspect carcinogens in conventional coal and fuel oil combustion sources. After an investigation of the Conventional Combustion Environmental Assessment data base, scientists at TRW, Inc. identified eight of the substances as having been reported in coal and fuel oil combustion emissions. These eight include arsenic, beryllium, cadmium, nickel, polynuclear aromatic hydrocarbons (PAH), 2,3,7,8-tetrachlorodibenzodioxin (TCDD), formaldehyde, and trichloroethylene. The absence of emission data for the remaining thirteen compounds, does not ensure that they do not (or cannot) exist in combustion effluents. Consequently, the potential of formation in combustion emissions was evaluated for the following compounds:

Acrylonitrile
Benzene
Diethylnitrosamine
Dimethylnitrosamine
N-nitroso-N-ethyl urea
N-nitroso-N-methyl urea
Asbestos

Ethylene dibromide
Ethylene dichloride
Ethylene oxide
Perchloroethylene
Vinyl chloride
Vinylidene chloride

For the thirteen listed substances to appear in combustion effluents, certain conditions must prevail:

(1) The substances exist as contaminants in a fuel and because of inefficient mixing go through the combustion zone unchanged.

(2) Precursors to the formation of these substances might exist in the fuel or be formed in the combustion process and thus lead to their formation.

For either situation to occur certain thermodynamic and kinetic factors must also exist. This study is concerned with the combustion of standard fuels, i.e., oil or coal, where fuel hydrocarbons are converted to CO_2 and H_2O, and not waste materials. For any of the substances to be produced at trace levels, chance factors, not derivable from normal thermodynamics and kinetics, must exist. Thus we can only estimate the probability of formation of these substances in significant amounts.

Recognizing that the emission data for the thirteen substances are essentially non-existent, we attempted to estimate the formation probability of these substances by examining: (1) thermodynamic stability, (2) related synthesis reactions, and (3) combustion formation conditions. Since asbestos is not formed as a result of actual combustion processes, only the origins of this mineral (e.g. liner insulation) are considered in the discussion of possible source discharges.

THERMODYNAMIC STABILITY

To estimate the probability of any of the 12 organic substances being present in the combustion of gas, oil, or coal, one must first ask, "What is the thermodynamic stability of the

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substance?" The stability of a compound at any temperature is measured by the free energy of formation of the compound at that temperature. The probability of formation depends on the sign and magnitude of the free energy. Compounds having a negative free energy of formation are thermodynamically favorable; the more negative the free energy of formation, the greater the probability of formation. Any substance with a positive free energy of formation near flame temperatures can be expected to completely dissociate. Hence the emission level under such conditions would be well below the parts per thousand (ppt) or even parts per billion (ppb) levels. If equilibrium is reached in the combustion system and if formation or destruction mechanisms exist, the equilibrium concentration of the compound can be deduced from the free energies of all the species involved and the concentrations of the reactants, as demonstrated by the following calculations for ethylene oxide.

The free energy ($\Delta F°$) of reaction for the oxidation of ethylene oxide at 1500°K is calculated as follows:

$$C_2H_4O + 3/2\ O_2 = 2CO + 2H_2O$$

$$\Delta F°_{1500}[C_2H_4O] = 42 \text{ kcal}$$

$$\Delta F°_{1500}[O_2] = 0 \text{ kcal} \qquad \text{(a)}$$

$$\Delta F°_{1500}[CO] = -58 \text{ kcal}$$

$$\Delta F°_{1500}[H_2O] = -39 \text{ kcal}$$

$$\Delta F°_{1500}[\text{Reaction a}] = 2(-39) + 2(-58) - 1(42) - 3/2(0) = -236 \text{ kcal.}$$

The equilibrium constant (Kp) for this reaction can be calculated as follows:

$$\Delta F° = -RT \ln K_p$$

$$K_p = \exp \frac{-\Delta F°}{RT} \qquad \text{(b)}$$

$$K_p, 1500 = \exp \frac{236000}{(2)(1500)} = 1.5 \times 10^{34}.$$

If a mixture of ideal gases is assumed, K_p is also equal to the following:

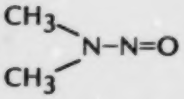
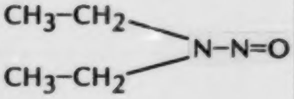
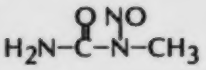
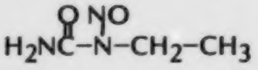
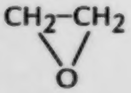
$$K_p = \frac{X^2_{CO}\ X^2_{H_2O}}{X_{C_2H_4O} X^{3/2}_{O_2}} P^{3/2} \qquad \text{(c)}$$

where X_i = volume fraction of i

P = total pressure of ≃ 1 atm.

The concentrations of CO, H_2O, and O_2 from typical combustion exhausts are approximately 0.1, 0.07, and 0.1 percent, respectively. The mole fraction of ethylene oxide from the equation above is 3×10^{-38}. Thus, knowing the thermodynamic properties of the reactants and products at a certain temperature, and the equilibrium concentrations of all but one species, one can estimate the concentration of the remaining species. In this case, a qualitative conclusion can be drawn that the emission level of ethylene oxide is insignificant compared to that of carbon monoxide. An inventory of thermodynamic data at 298 and 1500°K for the 12 organic substances under study is presented in Table 1. Except for some of the more common

TABLE 1. HEATS (ΔH°) AND FREE ENERGIES (ΔF°) OF FORMATION AT 298°K AND 1500°K (KCAL/MOLE) (1–4)

Substance	**Structure**	ΔH°_{298}	ΔF°_{298}	ΔF°_{1500}
Acrylonitrile (g)*	$H_2C=CH-CN$	44.1(2)	—	—
Benzene (g)	C_6H_6	19.8(3)	31.0(3)	—
Dimethylnitrosamine (l)**		1.1(4)		
Diethylnitrosamine		—	—	—
N-nitroso-N-methyl urea	 $H_2N-\overset{\overset{O}{\|}}{C}-\overset{\overset{NO}{\mid}}{N}-CH_3$	—	—	—
N-nitroso-N-ethyl urea	 $H_2N\overset{\overset{O}{\|}}{C}-\overset{\overset{NO}{\mid}}{N}-CH_2-CH_3$	—	—	—
Ethylene dibromide (g)	$BrCH_2-CH_2Br$	– 9.2(4)	-2.5(4)	—
Ethylene dichloride (g)	$ClCH_2-CH_2Cl$	-31.0(4)	-17.7(4)	—
Vinyl chloride (g)	$CH_2=CHCl$	8.5(4)	12.4(4)	—
Vinylidene chloride (g)	$CH_2=CCl_2$	0.6(4)	6.0(4)	—
Perchloroethylene (g)	$CCl_2=CCl_2$	-3.0(1)	5.2(1)	35.0(1)
Ethylene oxide (g)		-12.6(1)	-3.2(1)	42.1(1)

*"g" indicates that the substance is evaluated in the gas phase.
**"l" indicates that the substances is evaluated in the liquid phase.

substances, thermodynamic data are not available, particularly at higher temperatures. Methods are available to compute thermodynamic properties from statistical thermodynamics combined with correction factors for the various functional groups that compose the molecule. Such computations, although not within the scope of this study, would have limited benefit since they could only provide questionable estimates of overall combustion equilibria.

Except for perchloroethylene and ethylene oxide, the free energy of formation for the substances have not been reported; the same applies for the room temperature data of the nitrosamine and nitroso compounds. Heats of formation of acrylonitrile, benzene, dimethylnitrosamine, vinyl chloride, and vinylidene chloride at room temperature are positive and are expected to be even more positive at higher temperatures. Consequently, these substances are not thermodynamically favorable at 1500°K. The positive free energies of formation of perchloroethylene and ethylene oxide at 1500°K indicate that these compounds are not stable.

ORGANIC SYNTHESIS CHEMISTRY

Under ordinary conditions the 13 substances under study are not expected to be contaminants present in oil or coal. However, one must consider if these substances might be formed in the combustion process. The most logical manner of formation of these substances is via precursors. For simple molecules, such as NO, one would simply look for the possibility (thermodynamic and kinetic) of nitrogen and oxygen forming NO or of fuel-nitrogen species being oxidized to NO. Extending this rationale to the organics, one might say that as long as C, H, N, O, or Cl are present in the fuel, any or all 12 organics can be produced, a possible but most improbable conclusion. Thus, one might look for the possibility of simpler precursor molecules reacting in the flame or post-flame regions and leaving with the combustion gases. By way of a "clean" example, consider vinyl chloride, $CH_2{=}CHCl$. Most coals contain some chlorine. In the combustion process, even under excess O_2, some acetylene may be produced. Hence, one may visualize the following process:

$$\begin{gathered}\text{Coal Particle } (C, H, Cl \rightarrow C_2H_2, HCl, X, Y, Z) \\ C_2H_2 + HCl = H_2C{=}CHCl.\end{gathered} \tag{d}$$

Using such logic the 12 organics can be discussed in terms of logical synthesis routes. The routes or paths identified below are logical paths based on precursor routes from known organic syntheses, and cannot be considered as the only paths. It is not known if the precursors can be produced in flame or post-flame environments. Such a task, moreover, is outside the purview of this study since it would involve extensive analyses to establish the thermodynamic and kinetic probabilities of the precursors.

Acrylonitrile, $H_2C{=}CH{-}CN$

Acrylonitrile is extremely reactive, particularly in polymerization reactions and is produced via several pathways (5). The most probable route for the synthesis of acrylonitrile in a combustor would be the reaction of ethane, propane, or ethylene with hydrogen cyanide:

$$\left.\begin{array}{l} CH_3-CH_3 \\ CH_3-CH_2-CH_3 \\ CH_2=CH_2 \end{array}\right\} + HCN = CH_2=CH-CN + \text{------} \qquad \text{(e)}$$

The reaction is favored in the temperature range of 750 to 1000°C, and does not require the presence of a catalyst. To produce these hydrocarbon products and HCN, rich pockets of poorly mixed fuel and air are needed. Kinetics for these reactions are not available, but the reactions are probably very slow considering the low concentrations of hydrocarbon and HCN emitted from lean combustion systems. Until staged combustion procedures for NO_x control became standard practice, acetonitrile would be a more likely combustion product.

The addition of hydrogen cyanide to acetylene is possible, but the reaction has been studied only in a condensed phase under acidic conditions. Other less probable reaction paths require catalytic processes. Vapor phase catalytic reaction takes place at 400 to 500°C and at elevated pressures of 2.9 to 29 psig:

$$CH_2=CH-CH_3 + NH_3 + 3/2O_2 = CH_2=CH-CN + 3H_2O. \qquad \text{(f)}$$

The reaction produces hydrogen cyanide, carbon oxides, and acetonitrile as byproducts. In the same temperature range, the atmospheric reaction of isopropene and nitric oxide also proceeds, but in the presence of silver oxides or alkali metal oxides:

$$4CH_2=CHCH_3 + 6NO = 4CH_2=CHCN + 6H_2O + N_2. \qquad \text{(g)}$$

Acrylonitrile can also be formed from the catalytic dehydrogenation of ethyl cyanide at 550 to 650°C and atmospheric pressure; however, the catalysts required are chromium and vanadium oxide.

$$CH_3-CH_2-CN = CH_2=CH-CN + H_2. \qquad \text{(h)}$$

Although chromium and vanadium are found in raw coals and oils, and alkali metal oxides are generated during combustion reactions, reactions (g) and (h) will not proceed readily due to the required proximity and residence time at the catalyst surface. In general, all the reactions discussed are possible, recognizing, however, that all the identified organic precursors and HCN are readily oxidized under most normal flame conditions. Ammonia and nitric oxide should not be the limiting reagents, since they both are emitted from coal and oil-fired furnaces. Except for reaction (f), acrylonitrile formation is more likely to occur under reduced pressures.

Benzene, C_6H_6

The concentration of benzene in the stacks of conventional coal or oil-fired power plants has not been accurately measured, but substituted benzenes have been detected. Trace quantities of benzene and substituted benzenes are, of course, found in the exhaust of automobiles, the major source of the benzene products being the fuel. Data collected by Zelenski, *et al.* (6) on ethyl benzene, benzene, and 2,4-dimethylpentane are presented in Table 2. Relatively high concentrations are listed and the appearance of benzene in combustion emissions is very likely.

Although the catalytic cyclization and dehydrogenation of hexane could occur in a combustor, in a fuel such as coal, benzene is more likely formed from the thermal decomposition of the condensed polycyclic materials.

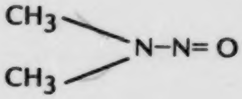
TABLE 2. TOTAL ORGANIC EMISSIONS FROM COAL-FIRED CONVENTIONAL PLANTS(6)

Compound	Concentrations	
	ng/J	ng/10^6BTU
2,4-dimethylpentane and benzene	1520×10^{-5}	3.5×10^{-5}
Ethyl benzene	2635×10^{-5}	6.1×10^{-5}

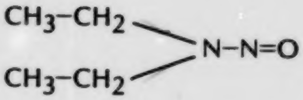
Nitroso Containing Organics

Structures for the four nitrosamines considered in this study are shown below.

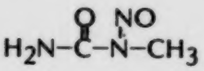
Dimethylnitrosamine



Diethylnitrosamine

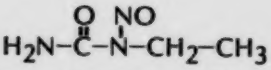


N-nitroso-N-methyl urea



$H_2N-\overset{\overset{O}{\|}}{C}-\overset{\overset{NO}{|}}{N}-CH_3$

N-nitroso-N-ethyl urea



$H_2N-\overset{\overset{O}{\|}}{C}-\overset{\overset{NO}{|}}{N}-CH_2-CH_3$

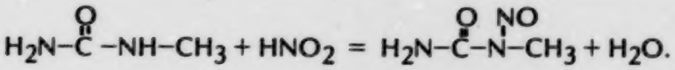
Dimethyl(ethyl)nitrosamine and N-nitroso-N-methyl(ethyl)urea have been studied extensively, originally in connection with nitrite-preserved foods such as bacon, bologna, smoked ham, and cheese. N-nitrosodimethylamine can be produced from the reaction of dimethylamine and nitrite. This compound has been found at concentrations up to 20 ppb in cooked bacon, although most N-nitrosodimethylamine is vaporized during cooking. In more recent examinations, N-nitrosamines have been observed in the surroundings of many chemical processing facilities, but not proven to be via combustion processes (7).

Two types of precursors are required to produce N-nitroso compounds. The amine fragment can be obtained from alkylated amines, amines containing carboxylic acids, or from substituted ureas. The nitrosyl portion may be derived from nitrous acid, nitrite salts, certain N-nitro compounds, and nitrogen oxides. N-nitrosation reactions can occur under acidic, neutral, or basic conditions. Formaldehyde, chloral, ozone, and metal ions are known to be effective catalysts.

For the four compounds that are of specific interest to the present study, dimethyl(ethyl)-nitrosamine are synthesized by reacting dimethyl(ethyl)amine with nitrous acid (or NO) at ambient conditions.

$$(CH_3)_2\,NH + HNO_2 = (CH_3)_2N{-}NO + H_2O. \qquad \text{(i)}$$

For N-nitroso-N-methyl(ethyl) urea, N-methyl(ethyl) urea is used:



$$H_2N{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3 + HNO_2 = H_2N{-}\overset{O}{\overset{\|}{C}}{-}\overset{NO}{\overset{|}{N}}{-}CH_3 + H_2O. \qquad \text{(j)}$$

Sodium nitrite ($NaNO_2$) is also a good nitrosation agent for dimethyl (ethyl)amine and N-methyl(ethyl) urea. Nitric oxide and nitrogen dioxide are stated to form nitrosated dimethylamine; the mechanism, however, is identified to be via reaction (i). The nitrous acid necessary for the reaction is believed to be produced by the heterogeneous reaction of nitric oxide and nitrogen dioxide with water on the reactor walls (8,9).

$$NO + NO_2 + H_2O = 2\,HNO_2. \qquad \text{(k)}$$

In the analysis of organics condensed on particulate matter in turbine engine exhaust, no trace of nitrosamines was detected. In this study, Robertson, *et al.* (10) were able to eliminate the possibility of nitrosamine formation because less than 1 percent of the organic matter emitted by the engine had been adsorbed. Furthermore, many nitrosamines of lower molecular weight are considered to be volatile. Since neither the dimethyl(ethyl)amine nor the N-methyl(ethyl) urea is readily generated from typical combustion reactions, the formations of dimethyl(ethyl)nitrosamine or N-methyl(ethyl)-N-nitroso urea is even less probable.

Volatile Halogenated Species

The structures of five halogenated organic compounds under study from the suspect carcinogen list are:

Ethylene dibromide	$BrCH_2{-}CH_2Br$
Ethylene dichloride	$ClCH_2{-}CH_2Cl$
Vinyl chloride	$CH_2{=}CHCl$
Vinylidene chloride	$CH_2{=}CCl_2$
Perchloroethylene	$Cl_2C{=}CCl_2$

In general, the major halogens identified with coal are chlorine and bromine. Chlorine is usually quite low in U.S. coal, less than 0.1 percent. If bromine is present, the levels are so low that they are rarely quoted. Regardless of amount, chlorine or bromine in fuels will be converted in combustion primarily to HCl or Cl_2 (or the bromine equivalent) depending on the hydrogen content of the fuel. Hence the key precursors will be HCl or Cl_2.

Ethylene dibromide and ethylene dichloride are formed from the bromination and chlorination of ethylene:

$$\begin{aligned} CH_2{=}CH_2 + Br_2 &= BrCH_2{-}CH_2Br \\ CH_2{=}CH_2 + Cl_2 &= ClCH_2{-}CH_2Cl. \end{aligned} \qquad (l)$$

However both compounds are unstable at high temperatures. At 340°C or above, ethylene dibromide decomposes in the presence of oxygen to form hydrogen bromide and vinyl bromide (5).

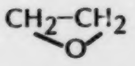
$$CH_2Br{-}CH_2Br = HBr + CH_2{=}CHBr. \qquad (m)$$

As a result, there exists a low probability for ethylene dibromide (chloride) emissions.

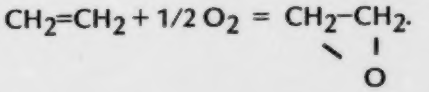
The probability of emission for vinylidene chloride, vinyl chloride, and perchloroethylene (in order of decreasing potential emission) cannot be excluded. Perchloroethylene is the least likely of the three to be formed because the four chlorine atoms in the molecule are sterically unstable. As illustrated earlier, vinyl chloride may be produced by reacting acetylene and hydrogen chloride.

Ethylene Oxide

Ethylene oxide whose formula is shown below has a low probability of occurrence.



Ethylene oxide is synthesized under conditions of low temperature and high pressure via the oxidation of ethylene (5).



$$CH_2{=}CH_2 + 1/2\,O_2 = \underset{\diagdown\ \ |\ \ \diagup}{CH_2{-}CH_2}\!\!\!\overset{}{}_{O}. \qquad (o)$$

A silver catalyst is needed for the reaction to proceed rapidly. However, at combustion conditions, the reaction of ethylene and oxygen to form carbon dioxide and water is thermodynamically favored:

$$CH_2{=}CH_2 + 3O_2 = 2CO_2 + 2H_2O. \qquad (p)$$

A probability of ethylene oxide emission still exists because of the presence of silver in coals and oils and the often met requirement of reduced oxygen concentration. These conditions will be found in the post-flame region; thus, reaction (o), forming ethylene oxide, is not eliminated.

Asbestos

Asbestos is discussed separately because it is not an organic molecule nor is it produced by a combustion reaction. Asbestos is a complex magnesium silicate. The most common form is chrysotile, a crystalline fiber with the empirical formula $Mg_3(Si_2O_5)(OH)_4$.

No information is available on the concentration of asbestos in stack gases, but if asbestos were to be observed it would probably result from insulation sloughed from the interior of furnaces (assuming it was used as a lining material) or possibly from an unusual contaminant in the fuel.

COMBUSTION CONDITIONS

The precursors and organic substances discussed in the previous section have been analyzed mainly in terms of organic synthesis procedures. The nature of their existence in the combustion process must also be considered. In general, the combustion process may be separated into three time-temperature regions.

Region	Temperature	Residence Time
Flame	2000-3700°F	0.05-1 sec
Convection section	600-2000°F	5-8 sec
Stack	300-600°F	Variable

Essentially the combustion chemistry takes place in the flame zone where the fuel hydrocarbons are converted to CO_2 and H_2O. Residence times are short, as low as 50 msec for a gas flame and possibly 1 second for a coal flame. At temperatures available in the flame, some dissociation occurs yielding measurable quantities of CO, which is usually but not totally oxidized to CO_2 at the lower temperatures and longer residence times in the convection section.

The thermodynamics and the synthetic precursor chemistry of the substances under study would indicate that, if formed, these substances would be formed in this intermediate temperature region of a conventional combustion unit. They would have the longer residence times needed for pyrolysis and oxidation to occur.

Since combustion processes are high-temperature, excess-air processes, pyrolysis reactions will be very limited. Combustion processes, however, are both kinetically and aerodynamically controlled. When one is concerned with formation of trace level species, mixing, especially micro-mixing, plays a significant role. Although the overall stoichiometry may be lean, micro-mixing limitations create fuel rich pockets. The extreme condition is a coal particle or a partially vaporized fuel drop. Pyrolytic reactions may proceed under these conditions.

Estimates of mixing efficiency and pyrolysis kinetics are beyond the scope of the present study; hence, we can only offer these as possible (but highly improbable) routes for producing the precursors and/or the 12 organic substances.

CONCLUSION

A substantive, objective ranking of the potential for the 12 organics and asbestos to be found in stack gases is not possible based on the available data. From a subjective point of view the 13 substances are ranked in Table 3 in a decreasing order of probability for appearing in combustion emissions.

TABLE 3. PROBABILITY RANKING FOR THIRTEEN SUSPECT CARCINOGENS IN CONVENTIONAL COMBUSTION SOURCES

Compound	Probability
Absestos	Reasonable
Benzene	Reasonable
Acrylonitrile	Low
Vinyl chloride	Low
Vinylidene chloride	Low
Perchlorethylene	Minimal
Ethylene dichloride	Minimal
Ethylene dibromide	Minimal
Ethylene oxide	Minimal
Diethylnitrosamine	Minimal
Dimethylnitrosoamine	Minimal
N-nitroso-N-ethyl urea	Minimal
N-nitroso-N-methyl urea	Minimal

Benzene is ranked with a reasonable probability because some evidence shows that it has been measured; asbestos falls into this category because many older furnaces have exposed asbestos linings. Acrylonitrile, vinyl chloride, and vinylidene chloride are ranked with a low probability because chemical logic exists for their precursors to be produced in oil and coal flames. The remaining eight substances are ranked with a minimal probability since no strong evidence suggests their formation in combustion processes.

SECTION 5

OVERVIEW OF EXISTING METHODOLOGY

INTRODUCTION

Numerous sampling and analysis techniques are available for determining the suspect carcinogens in water, air, soil, and other matrices. Few procedures, however, have been developed specifically for their determination in stationary conventional combustion sources. Consequently, existing sampling and analytical methods for the substances under study were reviewed and evaluated for potential application to combustion emissions. The reviewed methods were drawn primarily from sources considered to represent current state-of-the-art practice, such as handbooks, manuals, and research reports published by EPA, other government agencies, and recognized professional organizations. General sampling techniques and relevant analytical approaches are discussed in the following pages of this report. Specific methods for each suspect carcinogen along with reference physical data are presented in Appendices A through C.

GENERAL SAMPLING TECHNIQUES

Several criteria are inherent in the design of a sampling program for a particular substance. The program should provide representative samples with minimal deterioration and contamination. Samples should be collected in sufficient quantity for the level of detection of the analytical method. Consideration of on-site analysis versus sample stability is also important. When on-site analysis is impractical because of sophistication level or costs, sample handling and storage should become an integral part of the sampling program. Quality assurance procedures including comprehensive field audits should be implemented throughout sampling efforts.

In addition to these basic sampling criteria, the design of the actual sampling device must include specific characteristics such as: (1) simplicity of operation, (2) field durability, (3) reliable, reproducible operation, (4) convenient size for transport and installation, (5) compatibility with sampled environment, and (6) acceptable matrix for noninterfering sample collection. The sampling device should also provide accurate measurements of all necessary physical parameters to support the required emission calculation.

Based on these criteria, three major methods for sampling combustion emissions were compared: EPA Method 5 train (and adaptations), SASS train, and grab sampling.

EPA Method 5 Train

The EPA Method 5 train was developed for sampling total particulate emissions from combustion sources (1). This sampling train (Figure 1) consists of a heated probe (glass or stainless steel), a heated particulate filter, and a series of impingers cooled by an ice bath. In operating this train, the probe and filter are maintained at a specified temperature to prevent condensation (generally 120°C ± 14°C). The first two impingers usually contain water, the third impinger is empty, and the fourth impinger contains desiccant. The impingers are placed in an

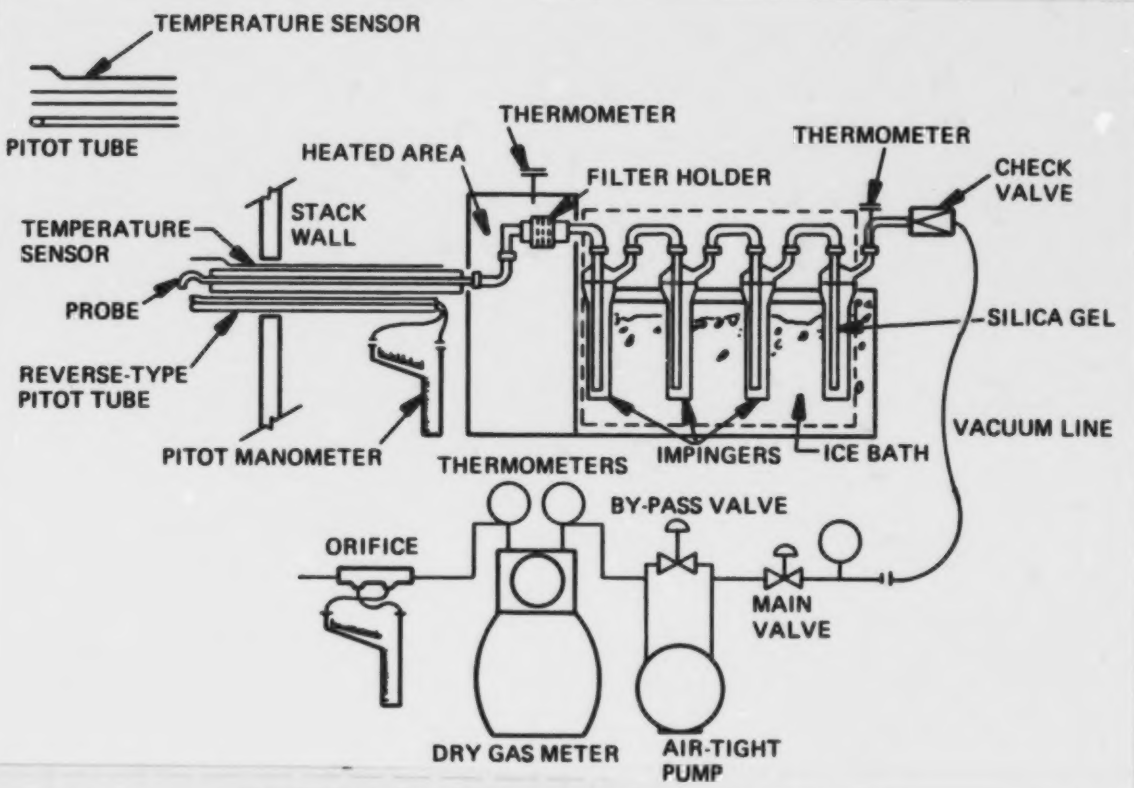

TEMPERATURE SENSOR
PITOT TUBE
HEATED AREA
THERMOMETER
FILTER HOLDER
THERMOMETER
CHECK VALVE
TEMPERATURE SENSOR
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
SILICA GEL
VACUUM LINE
PITOT MANOMETER
THERMOMETERS
IMPINGERS
ICE BATH
BY-PASS VALVE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

Figure 1. EPA Method 5 particulate sample apparatus.

ice bath to condense the moisture in the sampled gas. The gas is withdrawn by a vacuum pump usually at a rate of 1 cfm or less.

The Method 5 train has also been used for a number of other pollutant sampling programs. Method 8 is a modification of this train for SO_2 and sulfuric acid mist measurement. Method 13 is a modification for determination of total fluorides. EPA Method 17 is an adaptation of an ASTM Method using an in-stack thimble for collection of particulate material at stack temperatures (11).

The Method 5 train also has been modified to sample organic species by the addition of an organic adsorbing column. The method proposed for polychlorinated biphenyls (PCBs) by the EPA includes a solid adsorbent tube between impingers 3 and 4 of the Method 5 train (12). The tube is filled with 7.5 g of Florisil® to collect PCBs in the flue gas. A schematic diagram of this train is shown in Figure 2.

An additional Method 5 train modification involves the addition of a temperature-controlled adsorbent column after the heated particulate filter (13). This modified Method 5 train is used for collecting polycyclic organic compounds and can be enlarged to provide a sampling rate of 5 to 6 cfm. Diagrams of the train and the organic trapping column are presented in Figures 3 and 4, respectively. The organic trapping column contains an adsorbent to trap the substances of interest. A number of materials have been evaluated for sampling including activated carbons, Chromosorb 101, Chromosorb 104, Chromosorb W-HP, Porapak

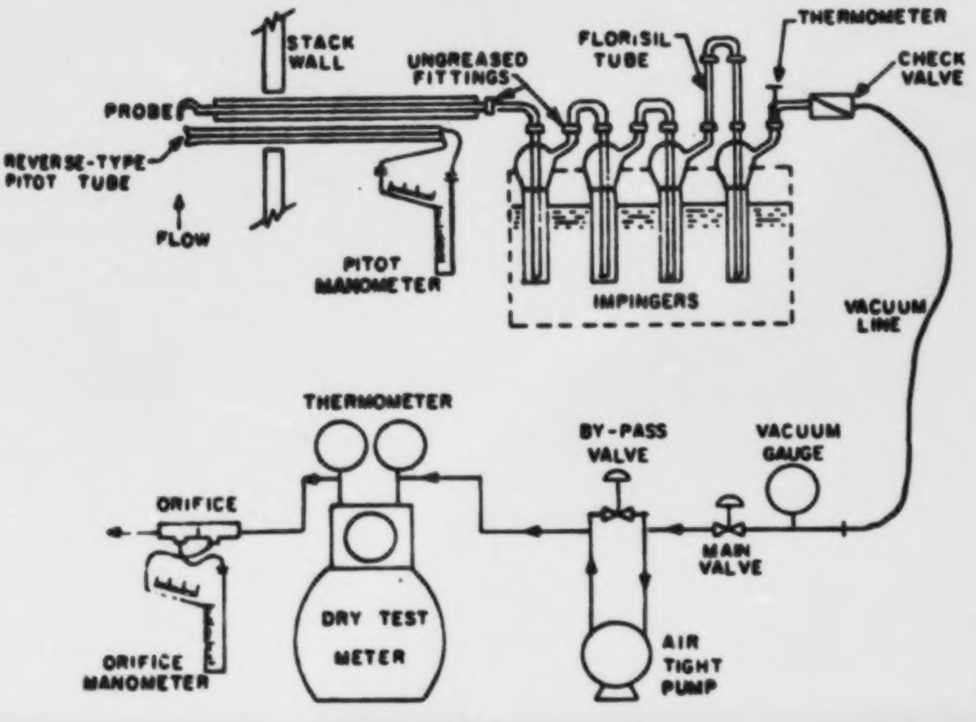

STACK WALL
UNGREASED FITTINGS
FLORISIL TUBE
THERMOMETER
CHECK VALVE
PROBE
REVERSE-TYPE PITOT TUBE
FLOW
PITOT MANOMETER
IMPINGERS
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY TEST METER
ORIFICE MANOMETER
AIR TIGHT PUMP

Figure 2. PCB sampling train.

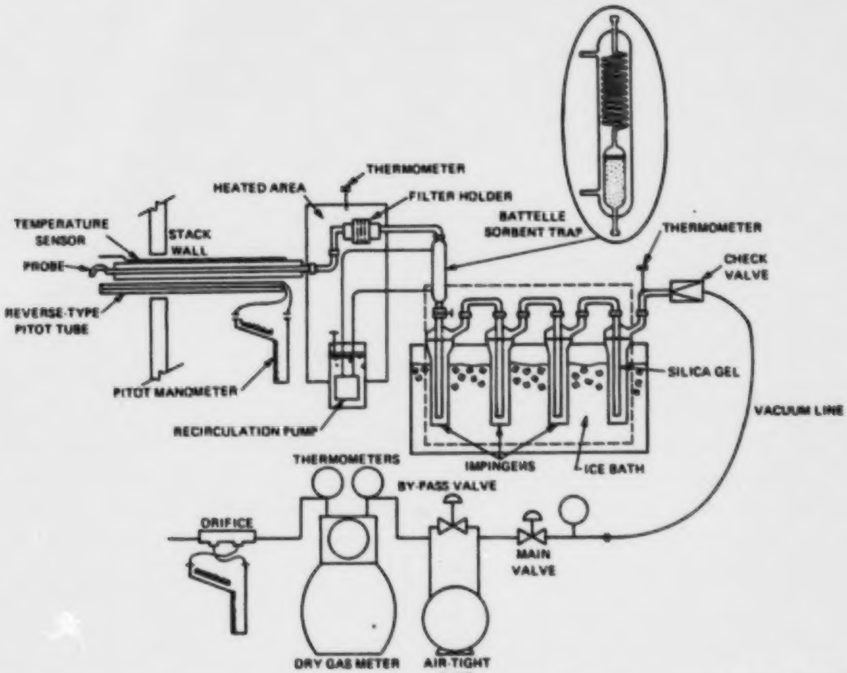

THERMOMETER
HEATED AREA
FILTER HOLDER
BATTELLE SORBENT TRAP
TEMPERATURE SENSOR
STACK WALL
THERMOMETER
PROBE
CHECK VALVE
REVERSE-TYPE PITOT TUBE
SILICA GEL
PITOT MANOMETER
VACUUM LINE
RECIRCULATION PUMP
THERMOMETERS
IMPINGERS
ICE BATH
BY-PASS VALVE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

Figure 3. Modified Method 5 train.

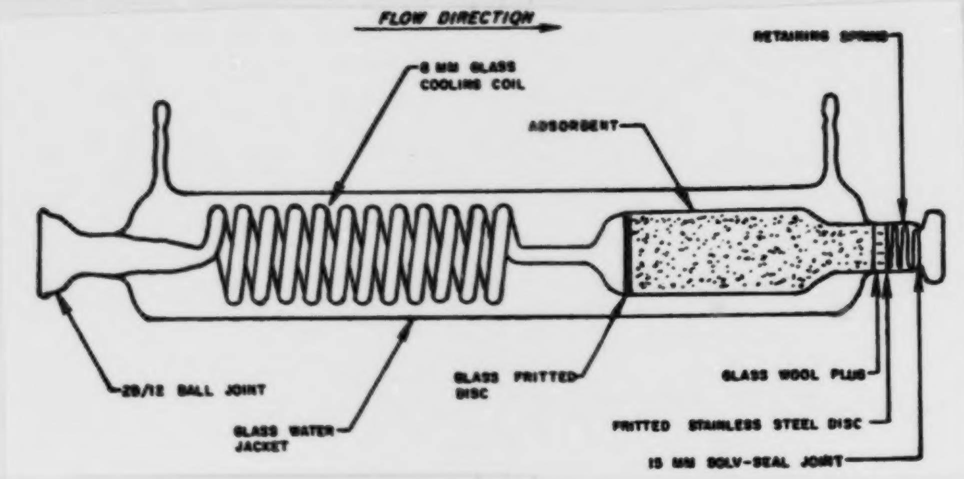

FLOW DIRECTION
8 MM GLASS COOLING COIL
RETAINING SPRING
ADSORBENT
28/12 BALL JOINT
GLASS WATER JACKET
GLASS FRITTED DISC
GLASS WOOL PLUG
FRITTED STAINLESS STEEL DISC
15 MM SOLV-SEAL JOINT

Figure 4. Basic trap for sampling organics in gas streams.

Q, and Tenax-GC (14). The most frequently used adsorbents are either Tenax-GC or XAD-2. The characteristics and use of these materials for sampling organics are discussed in U.S. EPA reports (15,16).

The standard Method 5 train can also include liquid trapping solutions in the impingers. A method of this type was developed for the U.S. Air Force for sampling dioxin from Agent Orange disposal operations (17). In this sampling system, benzene in the first two impingers was used to trap dioxins while activated charcoal in the third and fourth impingers trapped the benzene vapors. A schematic of this train is shown in Figure 5. This train was later modified to include four impingers containing benzene followed by silica gel and activated carbon impinger traps.

Another modification of the Method 5 train that uses liquid trapping solutions in the impingers is the midget impinger train. This train is similar in design to the Method 5 system except that the impinger volumes and sampling rates are reduced and the train uses a plug of

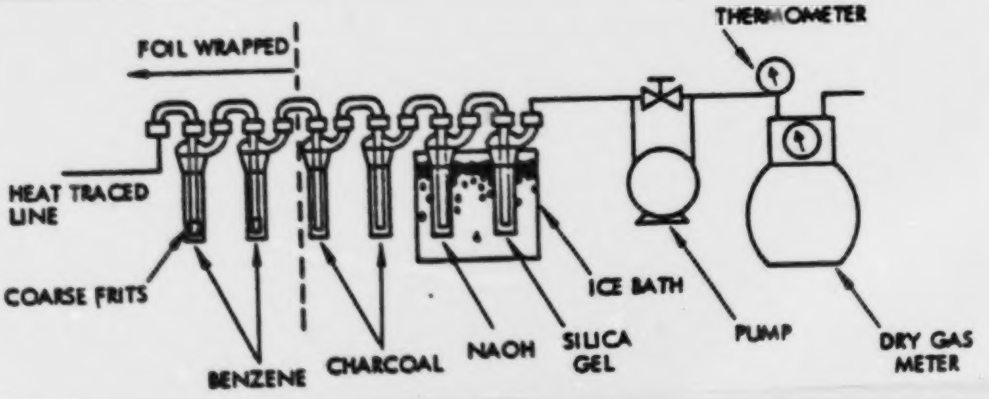

THERMOMETER
FOIL WRAPPED
HEAT TRACED LINE
COARSE FRITS
ICE BATH
PUMP
DRY GAS METER
BENZENE
CHARCOAL
NAOH
SILICA GEL

Figure 5. USAF impinger train for sampling dioxin.

glass wool instead of a filter to remove particulate material in the sampled gas. This type of train is specified in EPA Method 6 for SO_2 emission sampling (11).

A method for sampling aldehydes was developed using the midget impinger train (18). This train which uses an aqueous solution of 10 percent $NaHSO_3$ to trap aldehydes is shown in Figure 6. This method is an adaptation of the APHA Interscience Committee method for low molecular weight aliphatic aldehydes in ambient air (19).

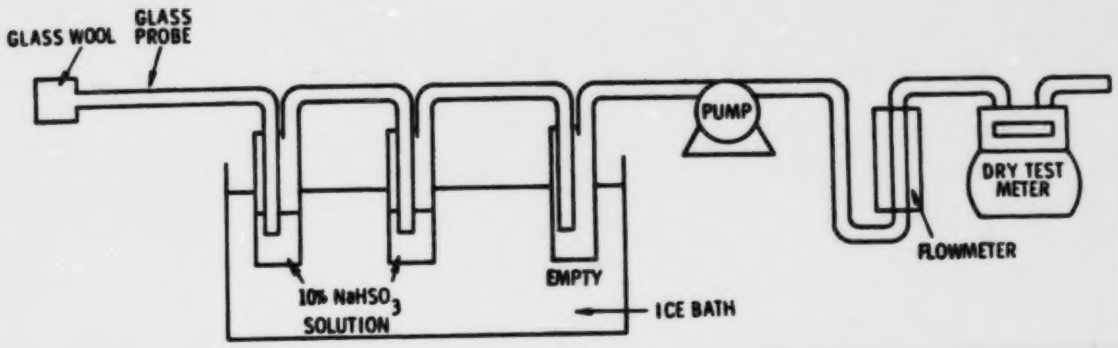


Figure 6. Diagram of sampling train for aldehydes.

SASS Train

The major limitations with most of the modifications of the Method 5 train are that they are either designed with a sampling matrix for a specific substance or group of substances and/or they sample at such a low flow rate that trace quantities of substances are not detected. The development of the SASS train provided a second major method of sampling source emissions that could provide samples suitable in both quantity and quality for extensive analysis as required for EPA programs.

The SASS train is shown schematically in Figure 7, and consists of a heated probe connected to a series of three cyclones and a filter that provides samples of size-partitioned particulate material. The cyclones provide nominal size cuts of 10 μm, 3 μm, and 1 μm at a flow rate of 0.113 sm^3/min (4.0 scf/min). The oven is heated to maintain a temperature of 204°C (400°F). Volatile vapors and gases pass through a temperature-controlled heat exchanger which cools the gas stream from 204°C to less than 20°C. The condensed vapors then pass through a resin trap containing approximately 150 g of precleaned XAD-2. The gas cooling unit also has the capacity to drain off the condensed liquid that has passed through the resin. The remaining volatile inorganics and gases pass through a series of impingers in an ice bath. The first three impingers contain solutions that trap the volatile inorganics (Hg, As, and Sb). The final impinger contains silica gel desiccant to remove any moisture remaining in the sampled gas.

The gas is pumped through the train by two high-capacity vacuum pumps in parallel (10 cfm capacity). EPA Level 1 Environmental Assessment procedures require a minimum sample of 30 standard cubic meters (20). These procedures also specify a number of other guidelines and criteria for sampling with the SASS train.

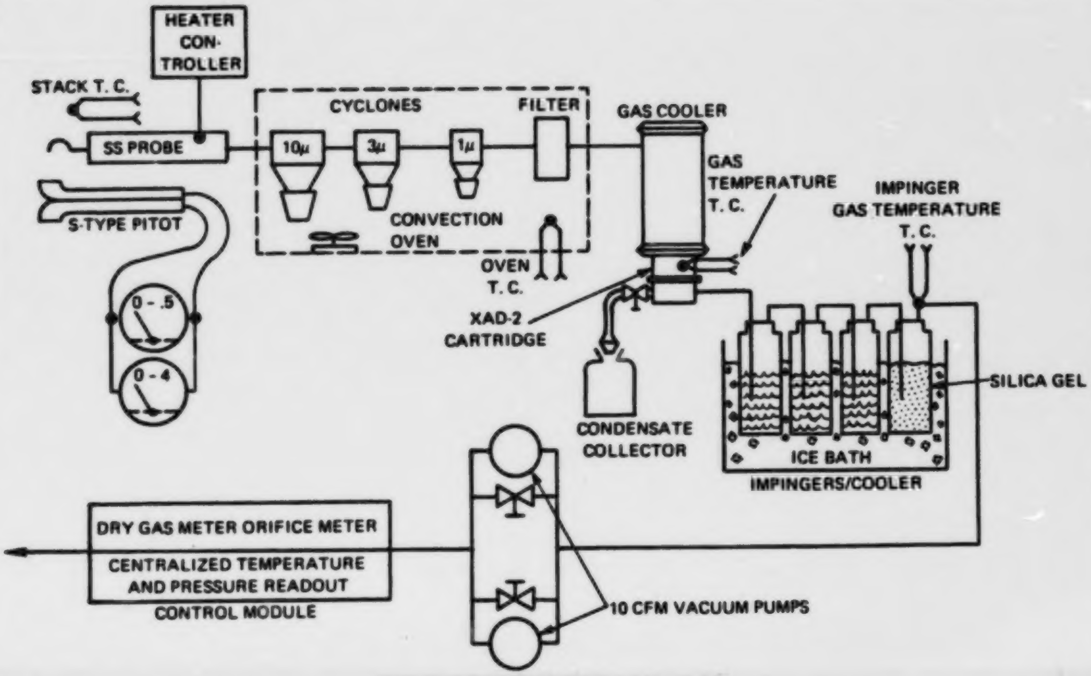

HEATER CON-TROLLER
STACK T. C.
SS PROBE
S-TYPE PITOT
0 - .5
0 - 4
CYCLONES
10μ
3μ
1μ
FILTER
CONVECTION OVEN
OVEN T. C.
XAD-2 CARTRIDGE
GAS COOLER
GAS TEMPERATURE T. C.
IMPINGER GAS TEMPERATURE T. C.
SILICA GEL
CONDENSATE COLLECTOR
ICE BATH
IMPINGERS/COOLER
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMPS

Figure 7. SASS train method.

The SASS train provides samples of size partitioned particulate material, condensed organics, and liquid trapped volatile inorganics. The particulate material may be analyzed for both inorganics and organic species but most organics are found in the resin trap. A schematic of the sample analysis from the SASS train is shown in Figure 8.

The resin trap is generally efficient for organic compounds with boiling points above 100°C (equivalent to a C_7 normal hydrocarbon). The application of XAD-2 for sampling with the SASS has been extensively investigated (21). A representation of the elution volume versus boiling point of the compound for groups of organics collected on XAD-2 resin is shown in Figure 9. The dotted line represents the SASS train operating conditions which indicate the limitations of this method for specific substances such as low-boiling, halogenated compounds.

EPA Level 2 Environmental Assessment procedures recommend that gases (boiling points less than 100°C) or vapors (boiling points greater than 100°C) which are not collected by the SASS train should be sampled by alternative methods (21). These methods should be EPA methods, if available, or other approved methods.

Grab Sampling

The third major method of air sampling, grab sampling, may be accomplished with evacuated flasks, evacuated bags, or simple traps. The evacuated flask is particularly suited for light hydrocarbon analysis. A schematic diagram of the system is shown in Figure 10. This method is limited by the size (maximum two liters) and possible nonintegration of the sample, but it does allow for onsite gas chromatography analysis.

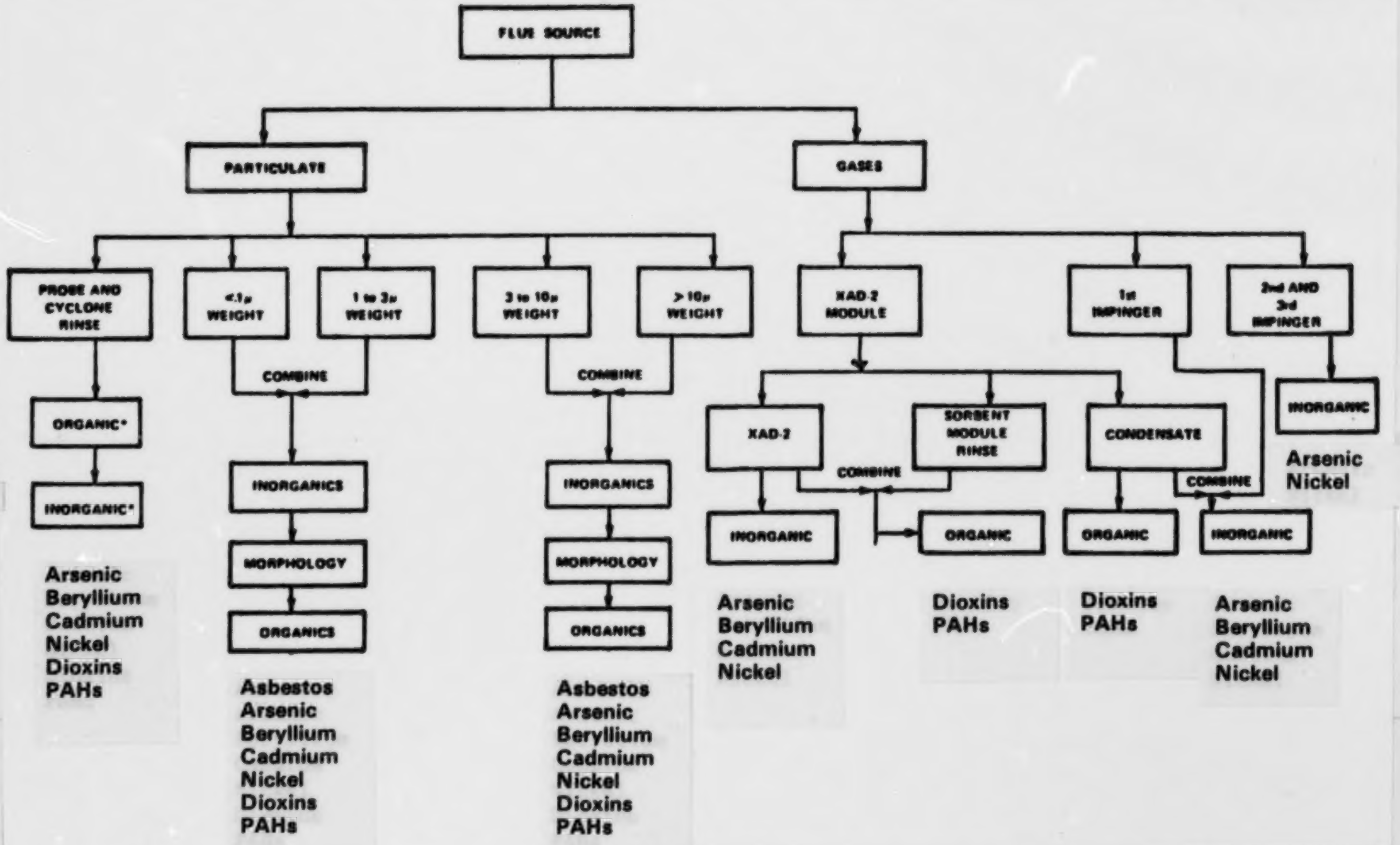

FLUE SOURCE
PARTICULATE
GASES
PROBE AND CYCLONE RINSE
<1μ WEIGHT
1 to 3μ WEIGHT
3 to 10μ WEIGHT
>10μ WEIGHT
XAD-2 MODULE
1st IMPINGER
2nd AND 3rd IMPINGER
ORGANIC*
INORGANIC*
Arsenic
Beryllium
Cadmium
Nickel
Dioxins
PAHs
COMBINE
INORGANICS
MORPHOLOGY
ORGANICS
Asbestos
Arsenic
Beryllium
Cadmium
Nickel
Dioxins
PAHs
COMBINE
INORGANICS
MORPHOLOGY
ORGANICS
Asbestos
Arsenic
Beryllium
Cadmium
Nickel
Dioxins
PAHs
XAD-2
SORBENT MODULE RINSE
CONDENSATE
COMBINE
INORGANIC
ORGANIC
ORGANIC
COMBINE
INORGANIC
INORGANIC
Arsenic
Beryllium
Cadmium
Nickel
Dioxins
PAHs
Dioxins
PAHs
Arsenic
Beryllium
Cadmium
Nickel
Arsenic
Nickel

Figure 8. Schematic of the sample analysis from the SASS train.

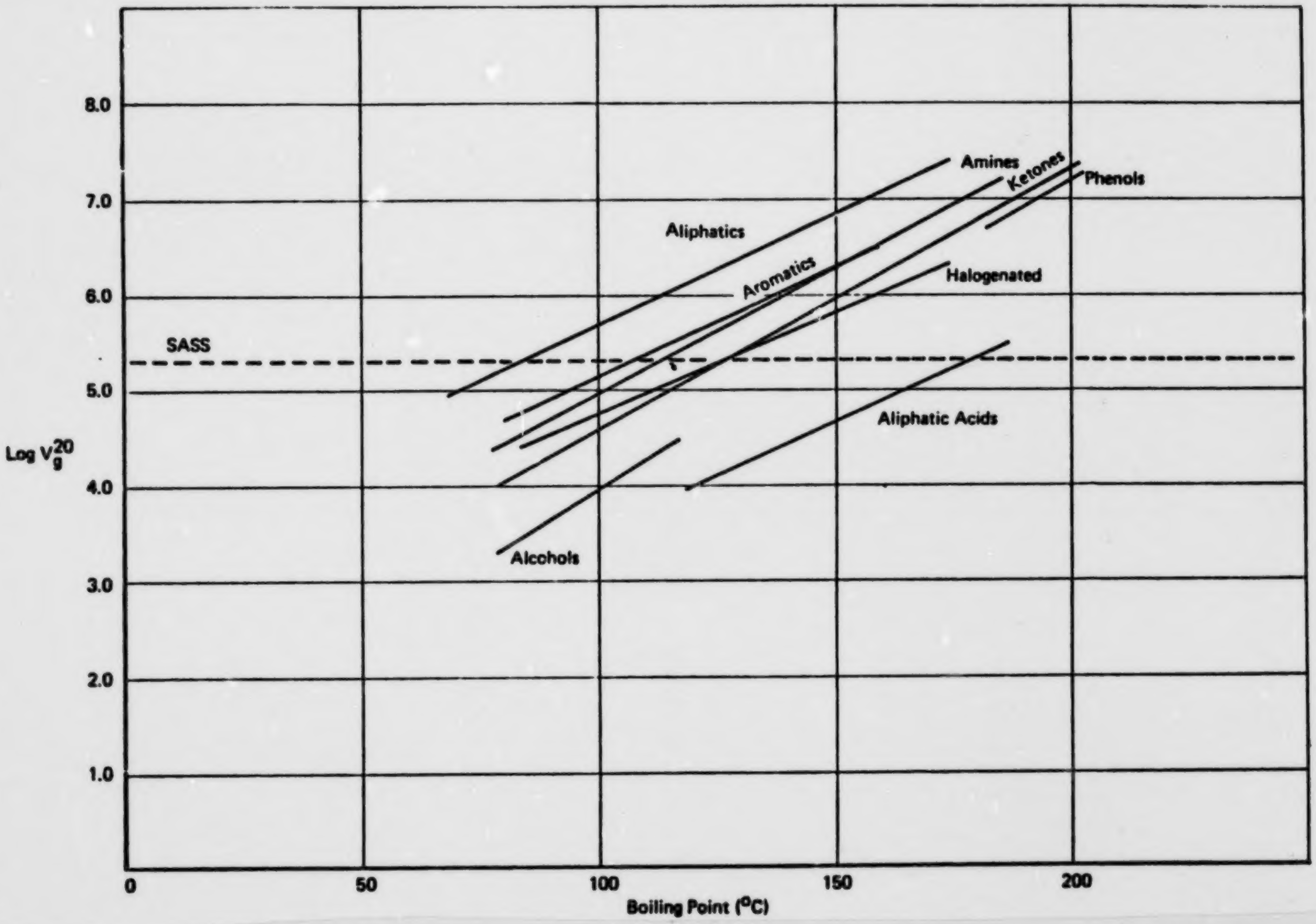


Figure 9. Log V_g° vs. boiling point for individual adsorbate groups on XAD-2. (The elution volume V_g° is the quantity in units of mL/g of gas sample at 20°C that can be passed through one gram of resin with very little breakthrough.)

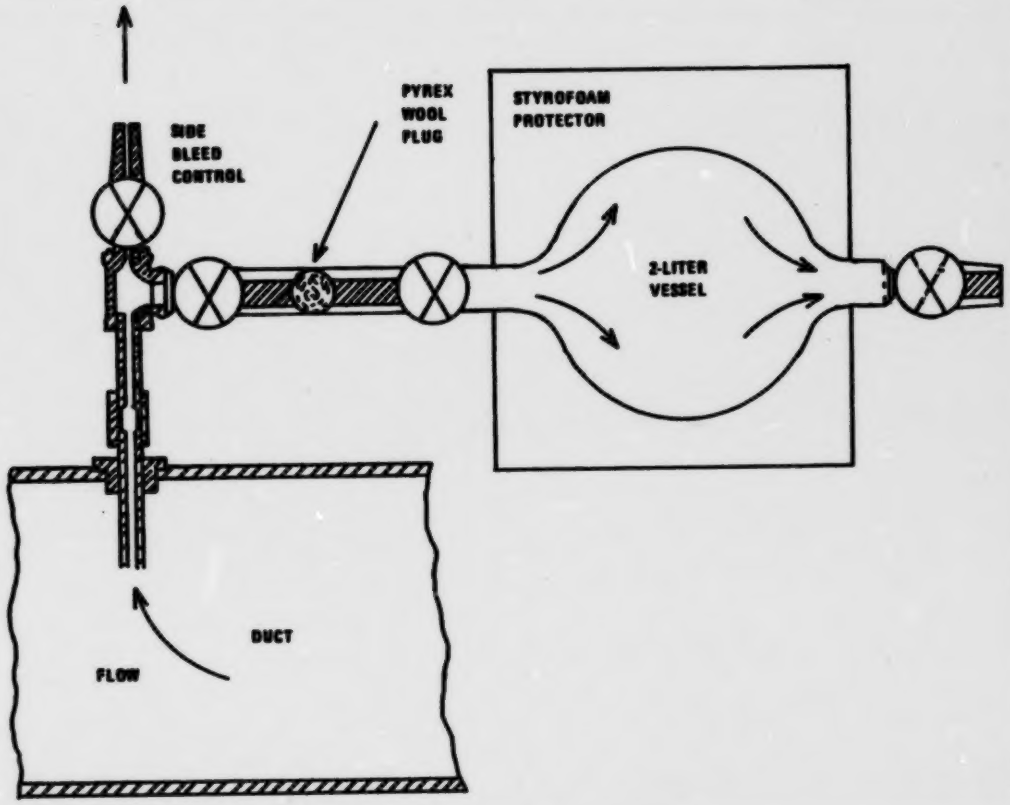

SIDE
BLEED
CONTROL
PYREX
WOOL
PLUG
STYROFOAM
PROTECTOR
2-LITER
VESSEL
DUCT
FLOW

Figure 10. Grab sampling apparatus.

The problems of sample size and sample integration are partially met by using an evacuated bag to sample the gas stream at a set flow rate. Two schematic diagrams of bag sampling systems are shown in Figures 11 and 12. The system shown in Figure 11 is specified for EPA Level 1 sampling for fixed gases (CO_2, O_2, N_2, and CO) and includes a Tedlar bag and a condenser to remove water vapor. The system in Figure 12 is specified in EPA Method 110 for benzene (22), Method 106 for vinyl chloride (21), and Method 23 for halogenated organics (23,24). Both systems provide samples up to 100 L. Problems with moisture, sample reactivity,

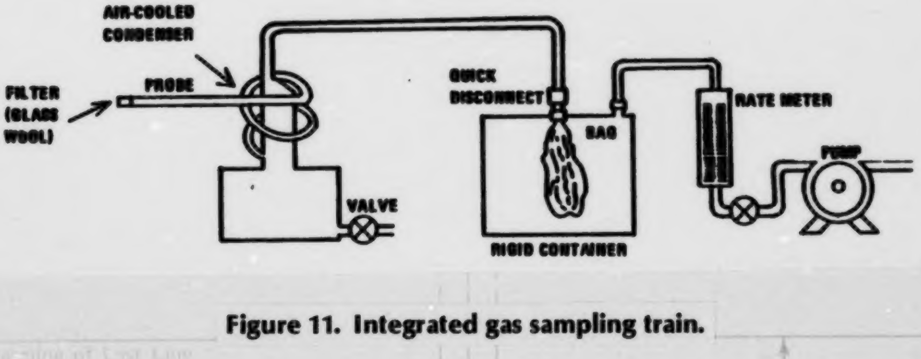

AIR-COOLED
CONDENSER
PROBE
FILTER
(GLASS
WOOL)
VALVE
QUICK
DISCONNECT
BAG
RIGID CONTAINER
RATE METER
PUMP

Figure 11. Integrated gas sampling train.

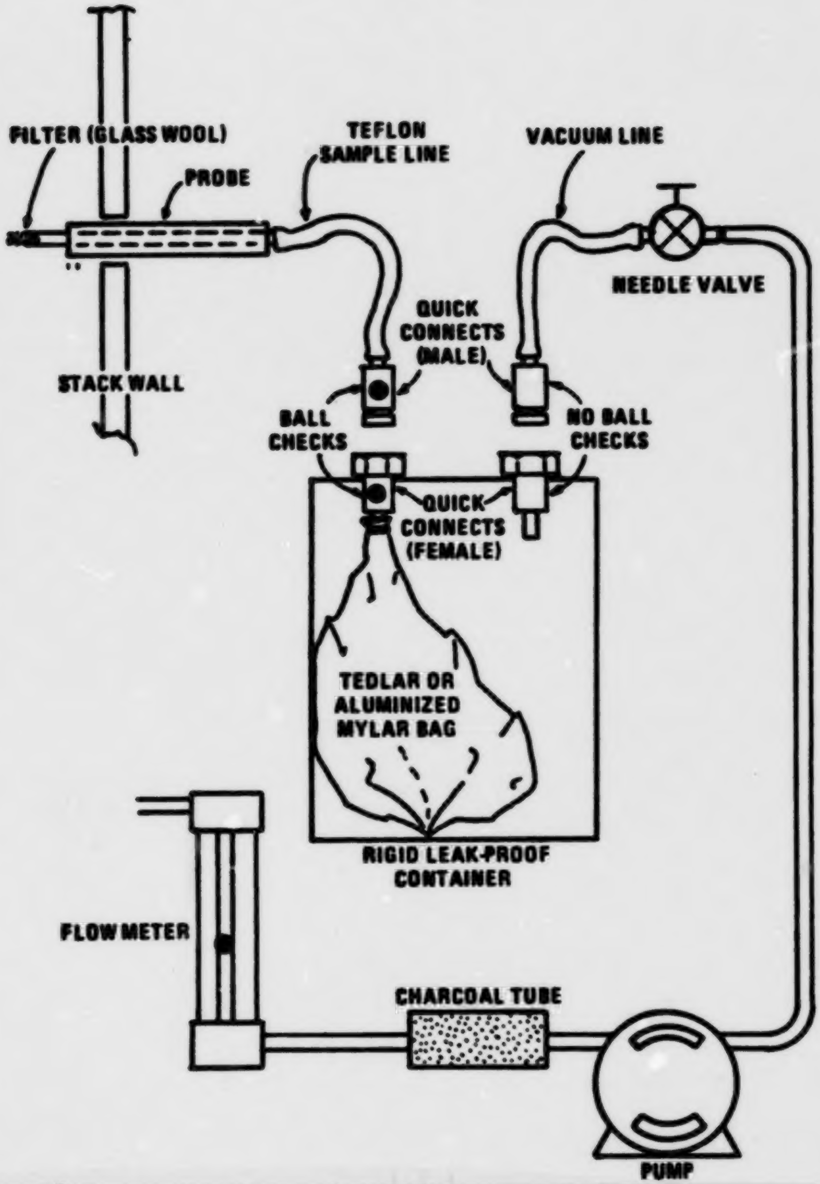

FILTER (GLASS WOOL)
PROBE
TEFLON SAMPLE LINE
VACUUM LINE
NEEDLE VALVE
QUICK CONNECTS (MALE)
STACK WALL
BALL CHECKS
NO BALL CHECKS
QUICK CONNECTS (FEMALE)
TEDLAR OR ALUMINIZED MYLAR BAG
RIGID LEAK-PROOF CONTAINER
FLOW METER
CHARCOAL TUBE
PUMP

Figure 12. Integrated bag sampling train.

degradation, permeability, and contamination have been found for a number of organic and inorganic substances (23,24,25). Consequently, for grab sampling with bags or flasks, the critical factors for any sampling program include: (1) the bag/flask material, (2) the holding time until analysis, and (3) protection from heat and sunlight. In a study of Tedlar bags for sample integrity, ethane, propylene, methyl chloride, and benzene were found to be stable for up to 14 days (25). A study of Tedlar bags for containment of benzene also showed no deterioration of sample except when the sample was heated to 150°C (22). In two other studies of the integrity of halogenated organics in Tedlar bags, trichloroethylene was found to remain stable for only 2 days and perchloroethylene for 10 days. Both ethylene chloride and ethylene bromide were found to be stable for less than 2 days (22,23). Vinyl chloride is reported to be stable for up to 3 days in Tedlar bags (26), but in charcoal tubes the stability is 7 days (27).

Sampling with a simple trapping device will provide a regulated volume of gas sample while retaining the sample integrity. This method is similar to the NIOSH methods which use charcoal tubes to trap organic vapors. A schematic of a trap sampling method for a source pollutant is shown in Figure 13.

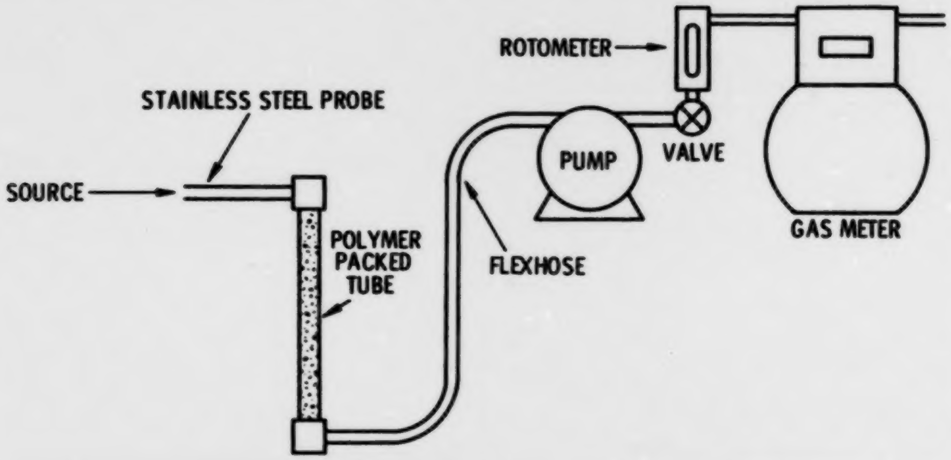


Figure 13. Porous polymer vapor sampling method.

This system would be suitable for low molecular weight organic gases or low boiling point vapors. The choice of adsorbent, which is critical for compound specificity and efficiency of recovery, depends on the species being adsorbed and on the sampling temperature, trap size, and elution volume of the substance. Other requirements for an adsorbent include: (1) high surface area, (2) particle size with minimal pressure drop, and (3) compatability with solvents. Generally, Tenax-GC would be used due to higher thermal stability. Other packings have been investigated but not necessarily for source sampling applications (27). Studies of the packed column shown in Figure 4 found that recovery of PAH, in addition to sorbent, was influenced also by column temperature, gas humidity, and organic loading (28). A Kaiser tube thermal gradient system has been proposed for compounds which have an extremely low elution volume at ambient conditions (21). This method is not generally used and still requires additional development.

Other methods of sampling are also available. Freeze trap methods may be used in either a sampling train or a grab sampling device. Rasmussen used a sample loop bathed in liquid oxygen to freeze out organics in air (29). The loop is heated and purged onto a gas chromatograph or mass spectrometer.

An adaptation of a sampling train using cryogenic trapping was demonstrated by Thomas (30). The sampling train consisted of a tared thimble for particulate (EPA Method 17) followed by a condenser and a dry ice freeze out trap. This train was used to sample benzo(a)pyrene (BaP) emissions.

One recently investigated method is the stack dilution sampling system (SDSS) (31). This system operates at a fixed sample to dilution air ratio with the result that particulate material is collected at ambient temperatures on tared 50 by 50 cm filters. Preliminary comparisions of the SDSS to the SASS indicate that the SASS is more suitable for organic emission characterizations but the SDSS may provide samples of particulate emissions which would be representative of atmospheric conditions.

GENERAL ANALYTICAL APPROACHES

Any analytical method for the suspect carcinogens in combustion emissions must be both reliable and accurate in view of the potentially hazardous nature of these compounds. In this regard, the EPA Enviromental Assessment Level 1 approach and EPA standard procedures were reviewed for applicability.

Level 1 Environmental Assessment

The phased approach to Environmental Assessment developed by the EPA Industrial and Environmental Research Laboratory involves comprehensive analysis—screening and analysis of overall sample components rather than seeking a limited list of preselected pollutants—and is therefore capable of providing useful screening information about suspect carcinogens if they are present in the emissions from a given source.

Level 1 analysis addresses the screening phase efforts. Level 1 was designed with the capability of providing information on any possible organic compound class and element present in a sample. Therefore, evidence for and sometimes actual identification of the members of the list of 21 suspect carcinogens is possible in a properly performed Level 1 analysis. In the standard Level 1 report format, the results would note the presence of the chemical class or element and provide an approximate concentration level for each class/ element identified.

The Level 1 procedures have not been evaluated in the laboratory for the 21 suspect carcinogens. Table 4 provides a summary of basic physical/chemical information for the sixteen organic compounds and shows how each organic compound relates to the Level 1 analysis scheme.

According to Level 1 procedures, volatile compounds (organic and/or inorganic) in effluent streams are collected and analyzed in the field. Eight of the organic compounds, if contained as major components in samples undergoing Level 1 assessment, could be identified and quantified in the field with some degree of confidence by comparison of the field GC data with the theoretical GC ranges outlined in Table 4. Confirmatory analysis, either by spiking a known member of the list into the field sample or by GC/MS analysis of the field sample (Level 2), would be required to identify a specific compound from the list.

In the case of higher boiling components, Level 1 procedures specify that Soxhlet extracts of combined sections of the SASS train undergo both total chromatographable organics (TCO) analysis for semivolatile organic compounds and gravimetric (GRAV) analysis for nonvolatile organic particulate matter. A liquid chromatographic fractionation (LC) is also conducted on each extract to separate complex mixtures into mixtures of simpler components for qualitative

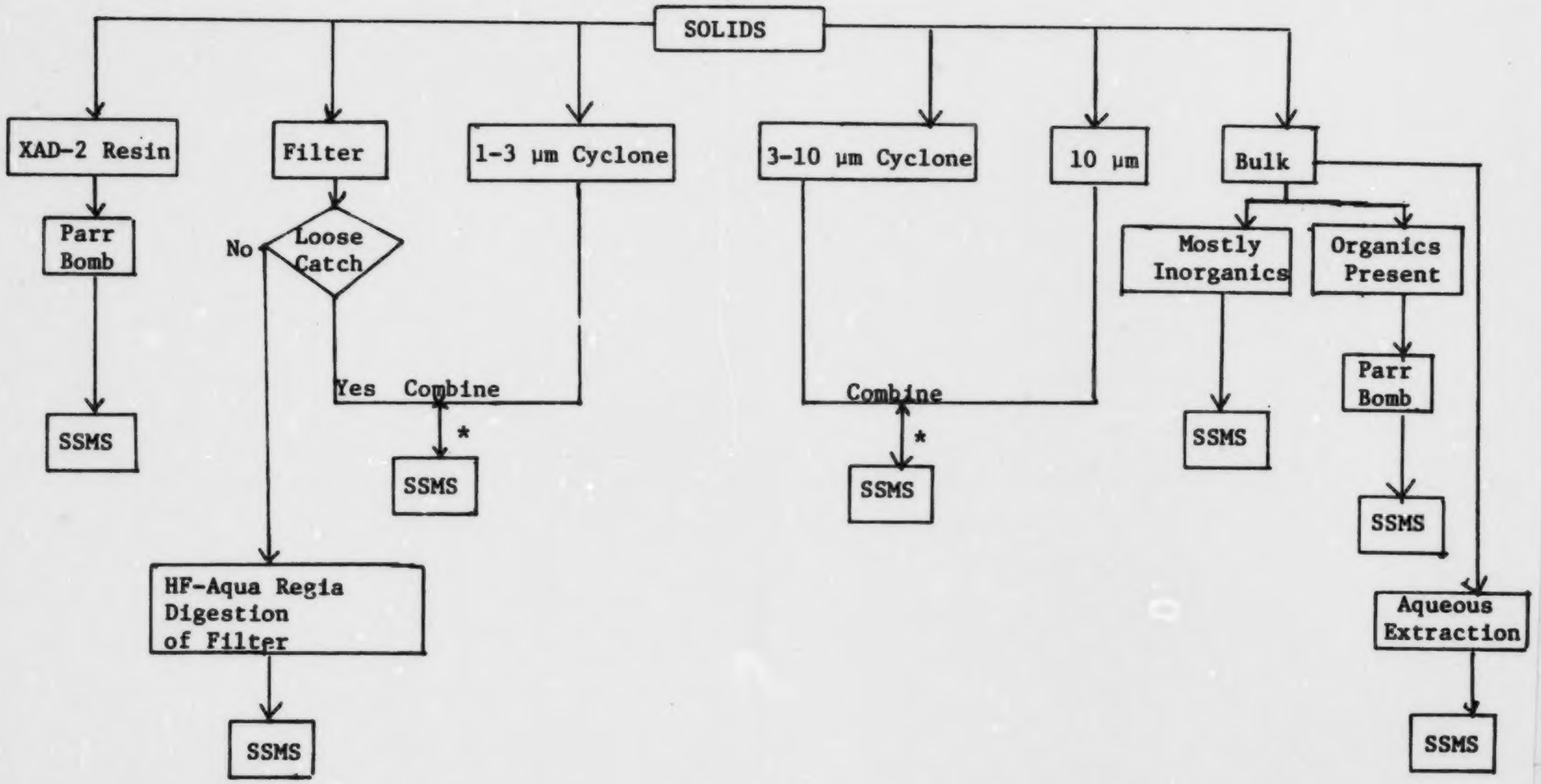
TABLE 4. LEVEL 1 ASSESSMENT

	Formula	Boiling	Air		GC Range								LC Fraction							
Compound	Weight	Point (°C)	Gas	SASS	1	2	3	4	5	6	TCO	GRAV	1	2	3	4	5	6	7	8
Acrylonitrile	53.06	77	●							●										
Benzene	78.11	80	●							●										
Diethylnitrosamine	102.14	176		●							●									
Dimethylnitrosamine	74.08	152		●							●									
Dioxin (2,3,7,8-TCDD)	321.09	00		●							●	●								
Ethylene dibromide	187.88	132		●								●								
Ethylene dichloride	98.96	84	●								●									
Ethylene oxide	44.05	11	●						●											
Formaldehyde	30.03	-21	●				●													
Nitrosoethylurea	117.11	103 (dec)		●							●									
Nitrosomethylurea	103.08	123 (dec)		●							●									
Perchloroethylene	165.85	121		●							●									
Benzo(a)pyrene	252.30	312 (10 mm)		●								●								
Trichloroethylene	131.37	87	●								●									
Vinyl chloride	62.50	-14	●				●													
Vinylidene chloride	96.94	32	●								●									

analysis by infrared (IR) spectroscopy and low resolution mass spectrometry (LRMS). Compound class and sometimes compound specific information is available from this procedure.

The four elemental species—arsenic, beryllium, cadmium, and nickel—may be identified in a number of samples within the Level 1 analysis scheme as Figures 14 and 15 demonstrate. Among solid samples, the four metals might be found in bulk solids or SASS train particulate samples. The SASS train samples would consist of the XAD-2 resin, the filter, and cyclone catches. In the XAD-2 resin, the metals would be identified by spark source mass spectrometry (SSMS) analysis after the resin has been properly treated in a Parr bomb (20). The filter catch is combined with the 1 μm cyclone catch and is analyzed by SSMS. The 3 μm and 10 μm cyclones are also combined and analyzed by SSMS. Analysis of bulk solids may also indicate the presence of the four inorganic suspect carcinogens. If the bulk material is composed primarily of inorganic components, then the solid is analyzed directly by SSMS. However, when significant quantities of organic matter are present, the bulk solid is treated in a Parr bomb prior to SSMS analysis. The bulk solids are also extracted with distilled, deionized water, and the metals may be found in the aqueous phase which is analyzed using SSMS.

In addition to solid samples, liquid samples may contain quantities of arsenic, beryllium, cadmium, or nickel. Liquid samples from production sources might include bulk liquids such as scrubber liquors, as well as SASS train samples: condensate from the XAD-2 module, the hydrogen peroxide impinger, and the ammonia persulfate (APS)/silver nitrate impingers. The bulk liquids and the combined condensate/hydrogen peroxide impinger are analyzed by SSMS. In the APS/$AgNO_3$ impingers, arsenic would be determined by atomic absorption spectrometry.



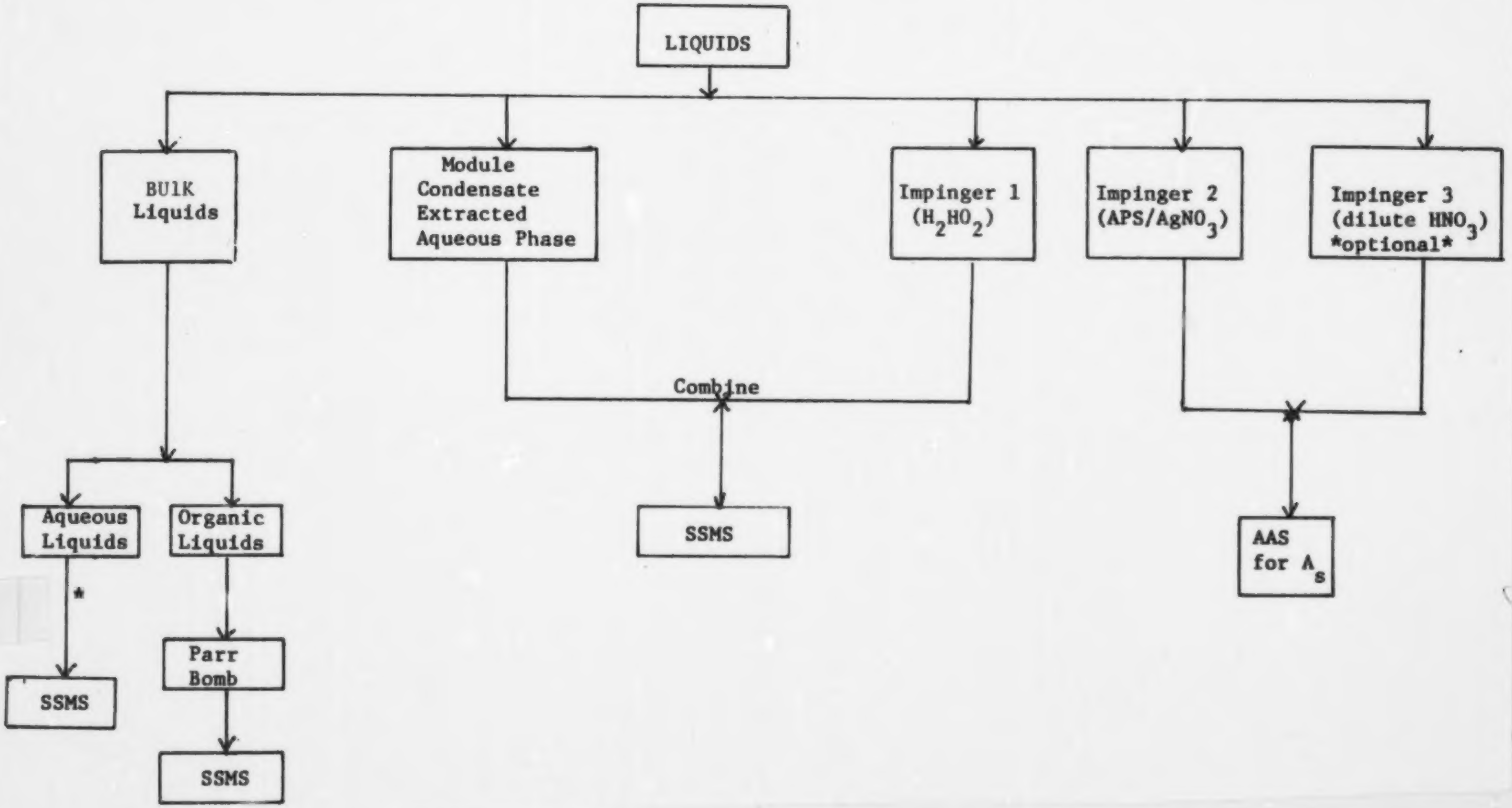

LIQUIDS
BUlK Liquids
Module Condensate Extracted Aqueous Phase
Impinger 1 (H_2HO_2)
Impinger 2 (APS/$AgNO_3$)
Impinger 3 (dilute HNO_3) *optional*
Combine
SSMS
AAS for A_s
Aqueous Liquids
Organic Liquids
*
SSMS
Parr Bomb
SSMS

Figure 15. Level 1 scheme for liquid samples.

The objectives of Level 1 analysis is to isolate the major classes of compounds present in a sample and to estimate their concentrations. Therefore, while specific compounds from the list of suspect carcinogens may not be identified, the possibility of their presence is shown by the presence of a class of compounds with similar characteristics. This situation makes the question of Level 1 detection limits somewhat complicated. One ppm of a given compound may be easily detected if it is a major component among other organics in the sample. If an isolated compound class is represented by one major component, then its detection limit can be more easily defined.

In the case of on-site gas chromatographic analysis, the detection limits are dependent upon the sensitivity of the gas chromatographic system used for the analysis and the interferences which may be encountered from source contaminants. According to Level 1 procedures (20), GC methods used for determining volatile concentrations have a sensitivity of one ppm (one mg per cu m in the gas stream samples) when no major interferences are present. Level 1 procedures provide quantitative data, but not qualitative data beyond the GC retention time of the peak in question. Qualitative identification of a given peak would require further laboratory analysis, such as GC/MS confirmation.

For all TCO and GRAV samples undergoing LC fractionation, LRMS is performed on each fraction or combined set of fractions if the total weight is greater than or equal to 15 mg. This decision criterion, when translated back to the source, yields threshold concentrations of 0.5 mg/m^3 for gases (ambient air, stack emissions, etc.) and 1 $\mu g/m^3$ for ambient air particulate. Since LRMS analysis is done on any LC fraction that corresponds to a source concentration greater than these threshold values, these values may be considered Level 1 detection limits for organics.

The analytical detection limits for the SSMS analyses of the four metals would be in the parts-per-billion (ppb) range. Arsenic in the APS/$AgNO_3$ impinger solution is quantified by the hydride generation method. The detection limit for arsenic is 2 ppb.

The important question about sensitivity of Level 1 methods for suspect carcinogens is whether or not the Level 1 procedures would qualitatively identify these compounds if present in the sample at the inner concentration level of concern. According to the Level 1 reporting procedure, a quantitative estimate would follow from the qualitative identification, LRMS intensity, and the TCO plus GRAV data for the sample.

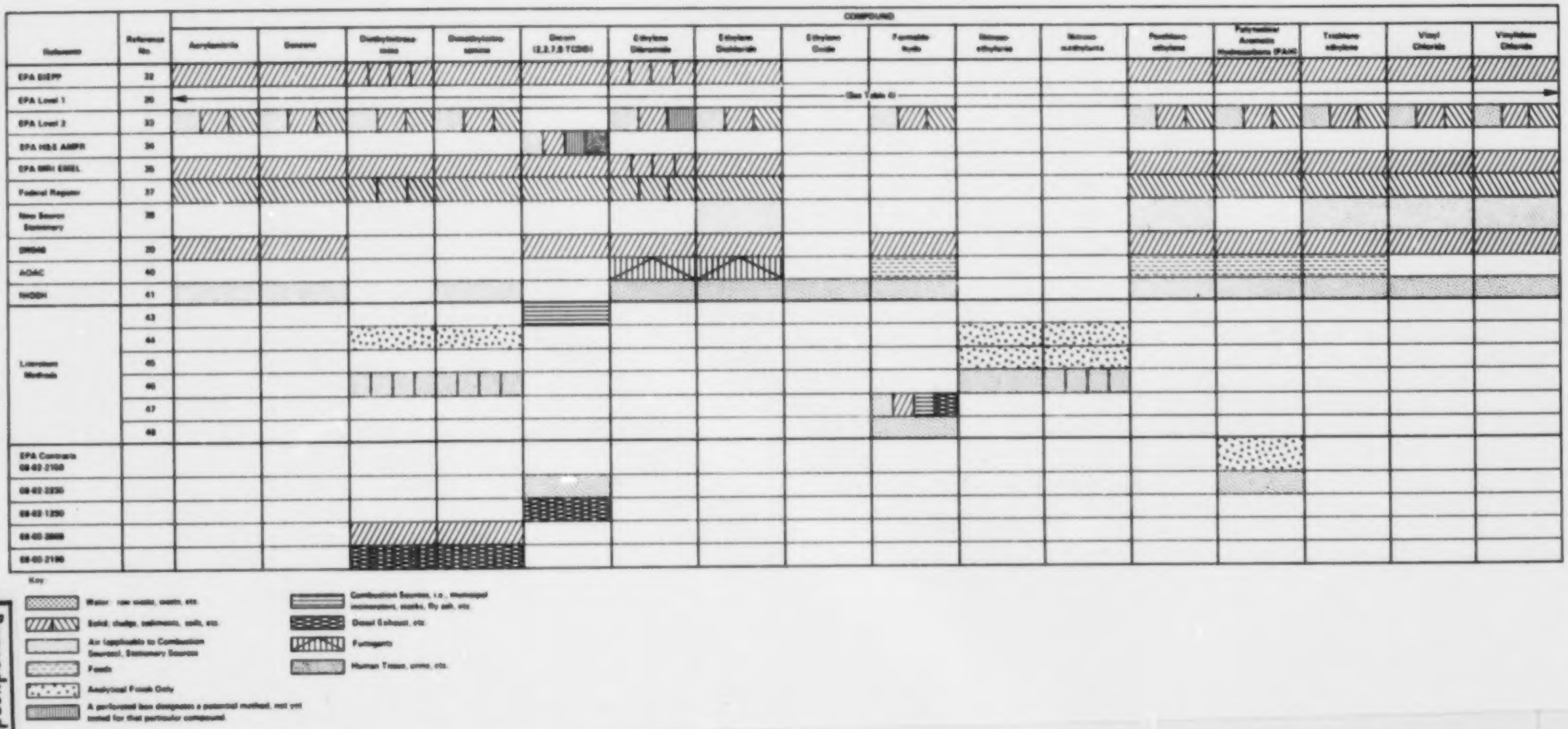
EPA Standard Methods

Organics—

The results of the search for EPA standard methods that would be applicable to the qualitative and quantitative determination of the organic suspect carcinogens from all sources appear in summary form in Table 5. Table 6 provides a key to the abbreviations representing standard EPA and other methods included in Table 5. In addition to this general summary, most of the methods in Table 5 are also cited in Appendices A through C for application with specific compounds.

In surveying Table 5, few standard methods apparently are designed explicitly for combustion sources. In general, most of the EPA standard methods are for sources such as air,

TABLE 5. STANDARD METHODS OF SAMPLING AND ANALYSIS ORGANIC SUSPECT CARCINOGENS



Source	Reference No.	COMPOUND Acrylonitrile	Benzene	Diethylnitrosamine	Dimethylnitrosamine	Dioxin (2,3,7,8 TCDD)	Ethylene Dibromide	Ethylene Dichloride	Ethylene Oxide	Formaldehyde	Nitroso-ethylene	Nitroso-methylurea	Perchloro-ethylene	Polynuclear Aromatic Hydrocarbons (PAH)	Trichloro-ethylene	Vinyl Chloride	Vinylidene Chloride
EPA SIEPP	32	▨	▨	▨	▨	▨	▨	▨					▨	▨	▨	▨	▨
EPA Level 1	20	← See Table 4 →															
EPA Level 2	33	░▨▧	░▨▧	░▨▧	░▨▧		░▨▥	░▨▧		░▨▧			░▨▧	░▨▧	░▨▧	░▨▧	░▨▧
EPA HSE AMPR	34					░▨▥▦											
EPA MRI EMSL	35	▨	▨	▨	▨	▨	▨	▨					▨	▨	▨	▨	▨
Federal Register	37	▧	▧	▧	▧	▧	▧	▧					▧	▧	▧	▧	▧
New Source Summary	38							░					░		░	░	░
ORGAS	39	▨	▨			▨	▨	▨		▨			▨	▨	▨	▨	▨
AOAC	40						▥	▥		┄			┄	┄	┄		
NIOSH	41	░	░		░		░	░	░	░			░	░	░	░	░
Literature Methods	43					☰											
	44			⁘	⁘						⁘	⁘					
	45										⁘	⁘					
	46			░	░						░	░					
	47									░▨☰▦							
	48									░							
EPA Contracts 68-02-2100														⁘			
68-02-2230						░								░			
68-02-1250						▦											
68-03-2608				▨	▨												
68-03-2196				▦	▦												

Key

- ░ Water - raw waste, waste, etc.
- ▨▧ Solid, sludge, sediments, soils, etc.
- ☐ Air (applicable to Combustion Sources), Stationary Sources
- ┄ Foods
- ⁘ Analytical Frame Only
- ▥ A perforated box designates a potential method, not yet tested for that particular compound
- ☰ Combustion Sources, i.e., municipal incinerators, stacks, fly ash, etc.
- ▦ Diesel Exhaust, etc.
- ▥ Fumigants
- ░ Human Tissue, urine, etc.

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TABLE 6. ABBREVIATIONS USED FOR CITATIONS IN TABLE 5

Abbreviation	Full Title	Reference
EPA SIEPP	"Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants"	32
EPA Level 1	"Procedures Manual: Level 1 Environmental Assessment"	20
EPA Level 2	"Methods for Level 2 Analysis by Organic Category"	33
EPA H & E AMPR	"Manual of Analytical Methods for the Analysis of Pesticide Residue in Human and Environmental Samples"	34
EPA MRI EMSL	"Measurement of Organic Priority Pollutants in Sludges and Sediments"	35
EPA MCA	"Methods for Chemical Analysis of Water and Wastes"	36
Federal Register	EPA Register of Federal Regulations	37
New Stationary Sources	EPA Register of Federal Regulations	38
SW846	"Test Methods for Evaluating Solid Waste"	39
AOAC	"Official Methods of Analysis of the Association of Official Analytical Chemists"	40
NIOSH	National Institute of Occupational Safety and Health Analytical Methods	41
Standard Methods	APHA/AWWA-WPCF	42
ASTM	"American Society for Testing and Materials"	49,50

water, wastewater, and solid waste. However, many of the analytical procedures could in principle be applied to combustion source samples after suitable sample preparation. The methods for ambient air analysis probably could be used for combustion sources with only a few simple modifications and therefore should be considered preferred candidate methods. Level 1 (20), Level 2 (33), NIOSH (41), and Federal Register New Stationary Sources (38) documents all contain candidate methodologies that have not yet been validated for these specific compounds in emissions from conventional combustion sources.

Some of the methods in Table 5 can also be used to determine more than one analyte at a time. Level 1 and Level 2 procedures fall under this category due to the fact that the SASS train enables satisfactory collection and subsequent recovery of all major categories of compounds. These methods are applicable to assessing samples from any of the air, water, or solid waste sources.

The Federal Register (37) discusses methods (601-625) which deal with analysis of water samples but which also describe analytical finishes for many of the organic suspect carcinogens. EPA Method 601 will determine five (probably six) of the halogenated hydrocarbons while EPA Method 624 will simultaneously determine these compounds plus acrylonitrile and benzene. In the Federal Register report on New Stationary Sources (38), reference methods 23 and 25 describe procedures for sampling and analysis of the six halogenated hydrocarbons from degasser and cold solvent cleaner emissions in the atmosphere.

Solid wastes such as sediment, soil, and sludge have been examined by the EPA Office of Solid Waste (OSW) (39). The several methods proposed by OSW are applicable to volatile organics (methods 8.01 and 8.24), volatile aromatics such as benzene (method 8.02), acrylonitrile, etc. (method 8.03) and polycyclic organic matter such as benzo(a)pyrene (methods 8.10 and 8.25), along with dioxin (2,3,7,8-TCCD) and corresponding isomers. EPA/MRI (35) discusses similar methods for many of the same compounds including the OSW methods. These methods enable simultaneous analysis of more than one analyte.

EPA has also conducted a study of sampling and analysis procedures for screening priority pollutants in aqueous industrial effluents (32). Once again, the halogenated hydrocarbons can be determined together as volatile organics; and dimethylnitrosamine, dioxin, and benzo(a)-pyrene can be measured together as base/neutrals.

Candidate sampling and analysis methods pertaining to ambient air or air pollution determination are of primary interest since these methods more closely apply to combustion source assessment. Based on this premise, four of the references cited in Table 5 appear appropriate. These include Level 1 and Level 2 procedures (20,33), Federal Register New Stationary Sources (38), and NIOSH (41). Each of these methodologies prescribes a sampling and analytical procedure for most of the suspect carcinogens. This information is outlined in Tables 7, 8, and 9 for each compound along with any additional criteria such as sample size, detection limits, desorption efficiencies, and precision values where they apply.

The Level 2 methodologies are based on Level 1 sampling procedures but rely on analytical finishes generally based on gas chromatography or HPLC methods. The principle of the Federal Register New Stationary Sources method which specializes in stack emission testing for halogenated organics is sample collection in an integrated bag sampling train and subsequent GC analysis. This method which is the same as the Level 1/Level 2 Method for volatiles (b.p. ≤ 100°C) does not apply to halogenated organics contained in particulate matter. There is also a newly revised method (106) for the specific determination of vinyl chloride from new stationary sources.

NIOSH (National Institute of Occupational Safety and Health) sampling methods consist of drawing the sampled air through a glass tube containing an appropriate solid sorbent, except in some cases such as formaldehyde where better recovery and stability are achieved with impingers. The sorbent is removed from the collection tube, desorbed with an organic solvent, and analyzed by gas chromatography, or occasionally HPLC.

Inorganics—

Table 10 presents EPA standard methods for the inorganic elements on the twenty-one suspect carcinogens list. Numerous methods for water, wastewater, and soils exist. These

TABLE 7. SUMMARY OF LEVEL 2 METHODS FOR ORGANIC COMPOUNDS

Compound	Sampling method	Sample size	Detection limit	Analytical finish
Acrylonitrile	Gas bulb/Grab	2L	250 ng	GC/FID; 3% SP1000 on 100/120 mesh Supelcoport
Benzene	Gas bulb/Grab	2L	2 ng	GC/FID; 0.1% SP1000 on 80/100 Carbopak C
Diethylnitrosamine	—*	—	—	
Dimethylnitrosamine	SASS/Sorbent	30 m^3	1 ng	GC/AFID; 3% SP2100 on 100/120 mesh Supelcoport
Dioxin	—	—	—	—
Dibromoethylene	—	—	—	—
Dichloroethylene	Gas bulb/Grab	2L	10 pg	GC/ECD; 0.2% Carbowax 1500/0.1% Carbopak C on 100/120 Supelcoport
Ethylene oxide	—	—	—	—
Formaldehyde	Impingers/MBTH solution	(Optional)	750 ng	Spectrophotometric
Nitrosoethylurea	—	—	—	—
Nitrosomethylurea	—	—	—	—
Perchloroethylene	SASS/Sorbent	30 m^3	10 pg	GC/ECD; 0.2% Carbowax 1500 0.1% Carbopak C
Benzo(a)pyrene	SASS/Sorbent + filter	30 m^3	10 ng	GC/MS; 3% Dexil 400 on 100/120 Chrom WAW
Trichloroethylene				GC/ECD; 0.2% Carbowax
Vinyl chloride	Gas bulb/Grab	2L	10 pg	GC/ECD; 0.2% Carbowax 1500/0.1% Carbopak C
Vinylidene chloride				

*A dash indicates that the Level 2 manual (10) includes no explicit reference to the indicated compound.

methods contain similar procedures in which ashed and/or diluted samples are analyzed by atomic absorption spectrophotometry (AAS) at the appropriate wavelength for each metal. For arsenic, the element is determined by an arsine generation procedure in the majority of these standard methods. For beryllium, cadmium, and nickel, both flame and flameless (graphite furnace) procedures are included among the standard methods.

Only the NIOSH methods (52) will provide information on the chemical speciation of the inorganic suspect carcinogens. These procedures have been validated for determination of five species of organic and inorganic arsenical contaminants in ambient air particulate samples. The collected particulates are extracted with a carbonate/borate buffer and the extract is passed through a Dionex ion-exchange column where the species are resolved. Quantification of the eluting species is carried out by arsine-generated atomic absorption analysis. Although this procedure is of considerable interest, its applicability to combustion sources must await development of reliable procedures for sampling such sources with preservation of arsenic speciation in the sample.

In 1980, EPA released a report entitled, "ICP/OES Procedure for Determining Trace Elements in Suspended Particulate Matter Collected on Glass Fiber Filters (1980 NAMS Procedure)". This method covers collection and analysis of As, Be, Cd, and Ni, among others, and employs inductively coupled plasma emission spectrometry (ICP). Particulate samples are collected on glass fiber filters, dissolved in a solution of nitric and hydrochloric acids with ultrasonication and heat, and analyzed by ICP. The ICP procedure has the advantage of simultaneous determination of beryllium, cadmium, and nickel with detection limits compar-

TABLE 8. SUMMARY OF NIOSH METHODS FOR ORGANIC COMPOUNDS

Compound	Collection Medium	Sample Size and Rate	Range and Precision of Method (mg/cum)	% Recovery/ Solvent	Analytical Finish
Acrylonitrile	Charcoal tube	20L @ 0.2 L/m	17.5–70.0±3.3	94% CH_3OH	GC/FID; Porapak Q
Benzene	Charcoal tube	2L @ 0.2 L/m	13.0–51.8±1.5	10% CS_2	GC/FID; Porapak Q
Diethylnitrosamine	—(a)	—	—	—	—
Dimethylnitrosamine	Tenax GC tube	5L @ 0.05 L/m	2.0–20.0±0.002	Thermal desorption	GC/AFID; 10% Carbowax 20M
Dioxin	—	—	—	—	—
Dibromoethylene	Charcoal tube	10L @ 0.2 L/m	110–470±16.9	92% CS_2	GC/FID; 10% FFAP
Dichloroethylene	Charcoal tube	10L @ 0.2 L/m	195–819±32	98% CS_2	GC/FID; 10% OV-101
Ethylene oxide	Charcoal tube	5L @ 0.05 L/m	41–176±9.3	99% CS_2	GC/FID; Porapak QS
Formaldehyde	Impinger pH 4.5	18L (8 hr T.W.A.)	1.44–6.16±0.16	104%	Girard T/Reagent/ polarography
Nitrosoethylurea	—	—	—	—	—
Nitrosomethylurea	—	—	—	—	—
Perchloroethylene	Charcoal tube	3L 2 0.2 L/m	655–2749±70.5	91% CS_2	GC/FID; 10% OV-101 on Supelcoport
Benzo(a)pyrene	Membrane Filter	0.5 2 2 L/m	0.02–0.80μg/m^3±(<10%)	—	TLC/Fluorometry
Trichloroethylene	Charcoal tube	3L 2 0.2 L/m	519–2176±88.2	94% CS_2	GC/FID; 10% OV-101
Vinyl Chloride	Activated	5L 2 0.05 L/m	1.27–71.3±(<5%)	100% CS_2	GC/FID; 10% OV-101
Vinylidene Chloride	Charcoal tube	7L 2 0.2 L/m	2.0–12.0±(<10%)	80% CS_2	GC/FID; 10% OV-101

(a) No method cited for this compound.

able to those of AAS. However, for arsenic, ICP has significantly higher detection limits than the arsine generation AAS procedure (0.5 ppb versus 5 ppb in aqueous solution, respectively).

Asbestos—

No standard or validated procedures for sampling asbestos from stack gases are available to date. However, a NIOSH recommended method of sampling and counting asbestos fibers consistent with Federal Regulations has been published by the Joint ACGIH-AIHA Aerosol Hazards Evaluation Committee (60). In this method, asbestos fibers are collected on a membrane filter which will retain particles larger than 0.5 μm at its surface. The filter is cut into wedges and dissolved in a 1:1 solution of diethyl oxylate and dimethyl phthalate. Subsequent counting of asbestos fibers is performed on a microscope equipped with a phase contrast condenser, a "high dry" phase-contrast objective, and a 10X eyepiece. A fiber is defined as a particle whose length is at least 3X its diameter. The range of the method is from 10 to 150 fibers per field. Research has been under way to find a way to automate the counting procedure and thus increase the accuracy of the method. Coulson, *et al.* (55) suggest the use of counting procedures that would provide identification, size distribution, and field counts. For this purpose, the use of electron microscopy is recommended.

TABLE 9. SUMMARY OF NEW STATIONARY SOURCE METHODS FOR ORGANIC COMPOUNDS

Compound	Sampling Method	Sample Time	Detection Limit	Precision, etc.	Analytical Finish
Acrylonitrile	—(a)	—	—	—	—
Benzene	—	—	—	—	—
Diethylnitrosamine	—	—	—	—	—
Dimethylnitrosamine	—	—	—	—	—
Dioxin	—	—	—	—	—
Dibromoethylene	—	—	—	—	—
Dichloroethylene	Integrated bag train	≤ 3 hours	Not determined	Not determined	GC/FID; 20% SP2100/0.1% Carbowax 1500 on 100/120 Supelcoport
Ethylene oxide	—	—	—	—	—
Formaldehyde	—	—	—	—	—
Nitrosoethylurea	—	—	—	—	—
Nitrosomethylurea	—	—	—	—	—
Perchloroethylene	Integrated bag train	≤ 3 hours	Not determined	Not determined	GC/FID; 0.2% SP2100/0.1% Carbowax 1500 on 100/120 Supelcoport
Benzo(a)pyrene	—	—	—	—	—
Trichloroethylene Vinyl Chloride Vinylidene Chloride	Integrated bag train	≤ 3 hours	Not determined	Not determined	GC/FID; 0.2% SP2100/0.1% Carbowax 1500 on 100/120 Supelcoport
Trichloroethylene	Integrated bag train	≤ 3 hours	Not determined	Not determined	GC/FID; 0.2% SP2100/0.1% Carbowax 1500
Vinyl Chloride	Integrated bag train	≤ 3 hours	0.02 ppm (injected)	3% Std. deviation at 2 ppm	GC/FID; Chromosorb 102
Vinylidene Chloride	Integrated bag train	≤ 3 hours	Not determined	Not determined	GC/FID; 0.2% SP2100/0.1% Carbowax 1500

(a) No method cited for this compound.

The basic NIOSH recommended method could possibly be adapted for application to combustion effluents. An alternative filter medium would be required for this application since the ester membrane filter is restricted to use at 75°C (170°F) or below. A glass or quartz fiber filter would probably not be acceptable because of likely interference in asbestos fiber counting. One of the fluorocarbon membrane filters (e.g., Millipore Mitex) may be adaptable for sampling of asbestos at stack gas temperatures as high as 250°C (480°F). Suitable procedures for recovering the fiber from a fluorocarbon membrane filter would need to be developed since these media will not dissolve in the oxylate/phthalate solvent. Once this aspect of the method is developed, the NIOSH asbestos procedure would be applicable for quantification of large fibers.

TABLE 10. STANDARD METHODS OF SAMPLING AND ANALYSIS FOR SUSPECT CARCINOGENS (INORGANICS)

Reference	Reference No.	Element			
		Arsenic	Beryllium	Cadmium	Nickel
EPA SIEPP	32	▒	▒	▒	▒
EPA Level 1	20	← (See Figures 14 and 15) →			
EPA MCA	36	▒	▒	▒	▒
SW846	39	▨		▨	▨
AOAC (12th ed.)	40	┄		┄	┄
NIOSH	41	░	░	░	░
Standard Methods (14th ed.)	42	▒	▒	▒	▒
ASTM 1975	49	▒		▒	▒
ASTM 1980	50		▤		▤
Literature Methods	51	▒	▒	▒	▒
	52	▤			
	53	▓			
	54	▨ ▒ ┄			
EPA Contracts: 650/4-74-015	55		▤	▤	
600/2-77-024	56	▤			
NAMS	57	▤	▤	▤	▤
68-02-1219	58	▤	▤	▤	▤
68-02-2443	59	▤	▤	▤	▤

Key:

▒ Water: raw waste, waste, etc.

▨ Solid; sludge, sediments, soils, etc.

░ Air (applicable to Combustion Sources), Stationary Sources

┄ Foods

∴ Analytical Finish Only

▥ A perforated box designates a potential method, not yet tested for that particular compound.

▤ Combustion Sources, i.e., municipal incinerators, stacks, fly ash, etc.

▩ Diesel Exhaust, etc.

◫ Fumigants

▓ Human Tissue, urine, etc.

SECTION 6

SPECIFIC SAMPLING AND ANALYSIS RECOMMENDATIONS

INTRODUCTION

Comparison and evaluation of the sampling and analysis methods presented in the preceding section of this report and in Appendices A through C led to the selection of optimum techniques for twenty-one suspect carcinogens in combustion emissions. These recommendations are described for each compound in the following pages and are cross-referenced to the report text in Table 11.

ORGANIC COMPOUNDS

Acrylonitrile

For acrylonitrile, the NIOSH approved method of collection on charcoal is recommended. Porous polymers do offer a feasible alternative to charcoal tubes; however these materials have not been validated for sampling acrylonitrile in emissions and the small sampling volumes used and potential artifact problems may make analysis difficult. The recommended analytical method is gas chromatography with flame ionization detection (GC/FID) or nitrogen specific detection. Mass spectroscopy could be used if specificity is necessary.

Benzene

Grab sampling with a gas bulb or Tedlar bag (EPA Method 110) is the recommended method for benzene in combustion emissions. GC/FID is recommended for analysis.

Dimethylnitrosamine, Diethylnitrosamine

Dimethlynitrosamine has the capability of being collected on charcoal according to NIOSH criteria. This capability should allow dimethylnitrosamine to be sampled in the XAD-2 sorbent module of the Level 1 SASS train. Diethylnitrosamine is assumed to have the same capability. Gas chromatography with alkaline flame ionization detection is recommended for analysis, although, as with the sampling method, this analytical finish has not been tested for diethylnitrosamine to date and its validity is only assumed.

Dioxin

Dioxins have been successfully sampled in fly ash from municipal incinerators by a method involving ultrasonic extraction of organics in benzene. A sorbent approach using a SASS train or Modified Method 5 train is recommended for stack gases. After sample preparation, gas chromatography combined with high resolution mass spectrometry (GC/HRMS) is the most recommended method for analysis.

TABLE 11. TEXT CROSS-REFERENCE FOR RECOMMENDED SAMPLING AND ANALYTICAL PROCEDURES

Compound	Sampling method	Text reference page	Analytical procedure	Text reference page
ORGANICS				
Acrylonitrile	Charcoal tube	84	GC/FID or GC/MS for specificity	84
Benzene	Tedlar bag/Gas bulb	89	GC/FID	89-91
Diethylnitrosamine	SASS train/Sorbent	43-44	GC/FID	43-44
Dimethylnitrosamine	SASS train/Sorbent	43-44	GC/FID	43-44
Dioxin	SASS/Modified Method 5 train	98	GC/HRMS	105-107
Ethylene dibromide	SASS train/Sorbent	43-44	GC/FID	43-44
Ethylene dichloride	Gas bulb	43-44	GC/ECD	43-44
Ethylene oxide	Charcoal tube	44	GC/FID	44
Formaldehyde	Impinger (DNPH)	115-116	HPLC, GC, or GC/MS for identification	118-120
Nitrosoethylurea	SASS train/Sorbent	35	HPLC with UV detection	35
Nitrosomethylurea	SASS train/Sorbent	35	HPLC with UV detection	35
Perchloroethylene	SASS train/Sorbent	44	GC/ECD	44
PAH	SASS/Modified Method 5 train	129-133	GC/LRMS	137-139
Trichloroethylene	Tedlar bag/Gas bulb	151-152	GC/FID	151-152
Vinyl chloride	Tedlar bag/Gas bulb	157	GC/FID	159-161
Vinylidene chloride	Tedlar bag/Gas bulb	157	GC/FID	158
INORGANICS				
Arsenic	Method 5 train/Modified Aerotherm HVSS system	169	Hydride Generation AAS	172
Beryllium	Method 5 train	180	AAS	182
Cadmium	Method 5 train	188	AAS	191
Nickel	Method 5 train	199-200	AAS	201-202
ASBESTOS	Filter	208-209	STEM	212-213

Ethylene Dibromide

Due to its semivolatile nature, ethylene dibromide may be collected in the Level 1 SASS train sorbent module. The validity of this collection method is based on the successful NIOSH method for sampling of ethylene dibromide on charcoal. The recommended analytical finish for this compound is GC/FID.

Ethylene Dichloride

Level 1 grab sampling in a bulb or bag is recommended for ethylene dichloride. This method allows rapid determination by field GC analysis which minimizes the loss of any of the compound due to air evaporation. The GC analysis should employ electron capture detection (GC/ECD).

Ethylene Oxide

EPA Level 1/Level 2 shows no proven method for the sampling and analysis of ethylene oxide. NIOSH, on the other hand, prescribes a typical method for this compound of adsorption onto charcoal and subsequent GC/FID analysis.

Formaldehyde

A method that employs collection and derivatization with DNPH (2,4-dinitrophenylhydrazine) and subsequent analysis by high performance liquid chromatography (HPLC) or gas chromatography appears to be the best approach for formaldehyde. Precise identification of formaldehyde can be achieved with GC/MS.

Nitroso-Ureas

The nitroso-ureas (nitrosoethylurea and nitrosomethylurea) by speculation only can be collected in the sorbent module of the Level 1 SASS train. Such methodologies have not been examined in regard to these compounds; therefore no data exist to back up the presumption. The analytical finish which would probably be most reliable is separation by HPLC and detection by UV at 264 nm. An HPLC/TEA (thermal energy analyzer) method is also worth mentioning, but has not been fully developed to a point where it can distinguish between specific types of N-nitroso compounds.

Perchloroethylene

A SASS train with an appropriate sorbent is recommended for perchloroethylene. The appropriate analytical finish would be GC/ECD.

Polynuclear Aromatic Hydrocarbons (PAH)

The sampling and analysis of polynuclear aromatic hydrocarbons (PAH) is achieved with a SASS train or Modified Method 5 collection system using XAD-2 resin trapping. High resolution capillary GC coupled with low resolution mass spectrometry (GC/LRMS) is recommended for analysis.

Trichloroethylene

Direct GC/FID analysis of a grab sample is recommended for the determination of trichloroethylene in combustion emissions.

Vinyl Chloride/Vinylidene Chloride

Of available sampling procedures for vinyl chloride and vinylidene chloride, grab sampling using gas bulbs, Tedlar bags, or charcoal adsorption tubes is recommended. The recommended procedure for analyzing these compounds is GC/FID (EPA Method 106).

INORGANIC COMPOUNDS

Arsenic

Sampling devices used to collect arsenic in combustion emissions may consist of a glass fiber filter and a nitric acid impinger system combined in a Method 5 train. A modified Aerotherm high volume stack sampler has also proven effective. The best analytical finish for arsenic is a hydride generation atomic absorption method.

Beryllium

For beryllium, EPA Method 104 is recommended. A Method 5 train containing a glass fiber filter and a nitric acid impinger series is used. The analytical finish prescribed is flame atomic absorption spectrophotometry (AAS) analysis of acid-digested samples (filter and impingers combined).

Cadmium

A Method 5 train with a glass fiber filter and nitric acid impinger system is also recommended for sampling cadmium. AAS should be used for analysis.

Nickel

For nickel, the Modified Method 5 train described previously, combined with flame AAS, is the recommended approach. The train can collect both volatile and nonvolatile nickel compounds.

ASBESTOS

Asbestos particles may be collected on a fluorocarbon membrane filter and isolated according to the methodologies discussed in the preceding section of this report. Both the SASS train and Method 5 train with either glass or quartz fiber filters should also be satisfactory for sampling, although no precedent for sampling and analysis of stack emissions for asbestos using these methods has been established. The use of a cellulose ester filter with transfer to polycarbonate filter is another possibility. For analysis, counting and identification by scanning transmission electron microscopy (STEM) has proven to be successful.

SECTION 7

COMPREHENSIVE FIELD STUDIES

INTRODUCTION

The specific sampling and analysis methods recommended in the previous section of this report are similar for several of the suspect carcinogens. To reduce the amount of effort required for determining the complete group of compounds in a single source emission, combinations of redundant techniques were considered. These combinations are reflected in the two comprehensive field studies described below.

FIELD STUDY USING EPA STANDARD METHODS

Based on the recommendations given in this report, the sampling and analysis procedures required for a comprehensive field study to determine the suspect carcinogens are summarized in Table 12. This proposed field study only accommodates those thirteen suspect carcinogens which have been reported or which have a medium to high probability of being present in combustion emissions as determined in Section 4 of this report. The inherent assumption in this study is that the eight substances ranked with a minimal probability are not present in combustion emissions, or that their presence is negligible in terms of potential hazards. The sampling system in this field study incorporates all EPA standard methods: (1) a SASS train or alternatively a high volume Method 5 train with an organic adsorbent column, (2) a midget impinger train for formaldehyde, and (3) an evacuated Tedlar bag sampling train with a by-pass charcoal tube for acrylonitrile. A schematic of this sampling system is shown in Figure 16. Specific operating and handling methods required to assure representative samples for analysis are discussed in the following sections for each of the sampling trains.

SASS Train

The operation of the SASS train is described in the EPA Level 1 Manual (20). To obtain a representative sample of the flue gas and particulate material, the sampling should be conducted at a point that is in compliance with EPA methods (61). Sampling at 8 duct diameters upstream from any disturbance and two duct diameters downstream from any ambient outlet point (or other flow disturbance) assures that the flow is uniform at the sampling point.

The sampling point for a SASS train is at a location of average flue gas velocity. The flue gas velocity and the stack gas volumetric flow rate are determined according to EPA Methods 1 and 2 using the stack gas velocity train. The velocity probe may be integral with the SASS probe or may be a separate system.

The sampling rate for the SASS operation is determined by the flow rate required for the particulate collection cyclones (0.113 sm^3/min). The SASS train sampling velocity in the flue gas is maintained at isokinetic conditions (−30 to +50 percent variance) by selecting a nozzle size based on the stack gas volumetric flow rate, the sampling rate, and the effluent water vapor content.

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TABLE 12. SUMMARY OF METHODS FOR COMPREHENSIVE FIELD STUDY

Compound	Collection matrix	Sampling method	Quantity of gas sampled	Analytical method	Interference
Asbestos	Particulate, filter	SASS/ HV-MM5*	30 sm^3	STEM	Other fibers
Arsenic	Impinger (H_2O_2)	SASS/ HV-MM5	30 sm^3	Hydride generation AAS	Excess H_2O_2, HNO_3
Beryllium	Particulate, filter	SASS/ HV-MM5	30 sm^3	AAS	
Cadmium	Particulate, filter	SASS/ HV-MM5	30 sm^3	AAS	
Nickel	Particulate, filter	SASS/ HV-MM5	30 sm^3	AAS	
Dioxin	Particulate/ resin/ condensate	SASS/ HV-MM5	30 sm^3	GC/HRMS	PCBs
PAH	Particulate/ resin/ condensate	SASS/ HV-MM5	30 sm^3	GC/LRMS	Organic Compounds
Trichloroethylene	Gaseous	Tedlar bag	100 liters	GC/FID	Particulate material
Vinyl chloride	Gaseous	Tedlar bag	100 liters	GC/FID	Particulate, acetaldehyde
Vinylidene chloride	Gaseous	Tedlar bag	100 liters	GC/FID	Particulate
Benzene	Gaseous	Tedlar bag	100 liters	GC/FID	Particulate, xylene, aldehydes
Formaldehyde	DNPH/HCl	Midget impinger train	120 liters	HPLC	Phenols, ethylene, propylene
Acrylonitrile	Charcoal	Tube	10 liters	GC/FID	

*HV-MM5 is a high volume Method 5 train modified with an organic adsorbent column.

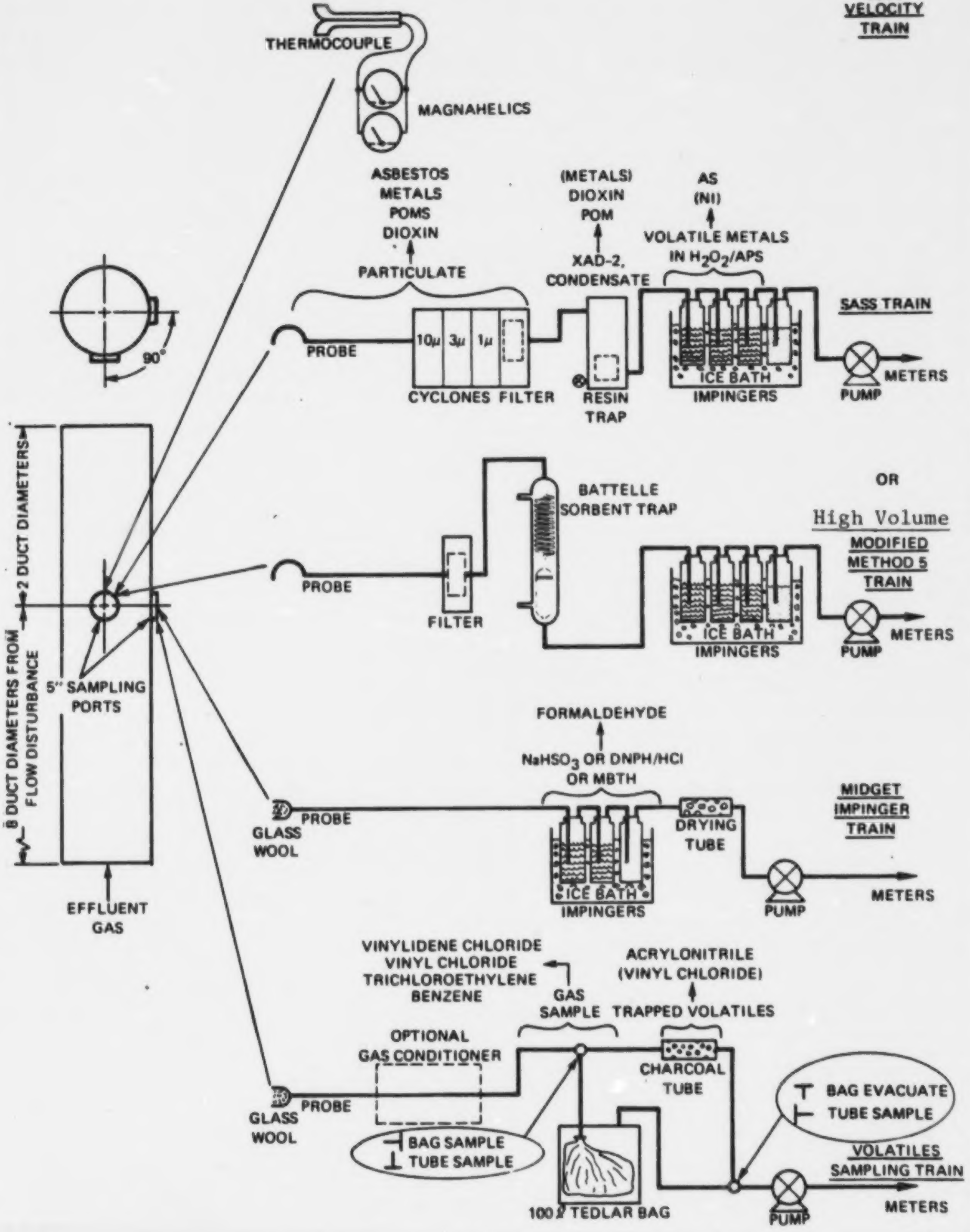
TC
THERMOCOUPLE
GAS VELOCITY TRAIN
MAGNAHELICS
ASBESTOS
METALS
POMS
DIOXIN
PARTICULATE
(METALS)
DIOXIN
POM
XAD-2,
CONDENSATE
AS
(NI)
VOLATILE METALS
IN H_2O_2/APS
SASS TRAIN
90°
PROBE
10μ
3μ
1μ
CYCLONES FILTER
RESIN TRAP
ICE BATH
IMPINGERS
PUMP
METERS
2 DUCT DIAMETERS
8 DUCT DIAMETERS FROM FLOW DISTURBANCE
5" SAMPLING PORTS
BATTELLE SORBENT TRAP
OR
High Volume
MODIFIED METHOD 5 TRAIN
PROBE
FILTER
ICE BATH
IMPINGERS
PUMP
METERS
FORMALDEHYDE
$NaHSO_3$ OR DNPH/HCl
OR MBTH
MIDGET IMPINGER TRAIN
GLASS WOOL
PROBE
DRYING TUBE
ICE BATH
IMPINGERS
PUMP
METERS
EFFLUENT GAS
VINYLIDENE CHLORIDE
VINYL CHLORIDE
TRICHLOROETHYLENE
BENZENE
GAS SAMPLE
ACRYLONITRILE
(VINYL CHLORIDE)
TRAPPED VOLATILES
OPTIONAL GAS CONDITIONER
CHARCOAL TUBE
GLASS WOOL
PROBE
BAG SAMPLE
TUBE SAMPLE
BAG EVACUATE
TUBE SAMPLE
VOLATILES SAMPLING TRAIN
100 ℓ TEDLAR BAG
PUMP
METERS

Figure 16. Sampling system for comprehensive field study.

The Level 1 sampling program is designed to collect 30 sm^3 of dry flue gas. The completion of sampling for a Level 1 test program requires at least 5-6 hours (dependent on water vapor content in the flue gas and actual flow rate through the train). This sampling time may be extended if high particulate loadings in the stack require frequent filter or cyclone changes.

The handling procedures for SASS operation are also specified in the EPA Level 1 Manual (20). The integrity of the collected samples is verified by (1) leak checking the sampling system to within specified tolerances, (2) maintaining train module temperatures within specified ranges, and (3) use of good laboratory practices in recovery of samples. The program also includes provisions for quality control by including representative blanks of all reagents and solvents.

High Volume Modified Method 5 Train

The alternative to the SASS train is a high volume Method 5 train modified with an organic adsorbent column (HV-MM5). This train differs from the SASS train because (1) no provision for particle sizing is available, (2) the XAD-2 sorbent column is of a different design, and (3) the system is generally an all glass system (compared to the SASS which uses 316 stainless steel).

The operation of this train is similar to that of the SASS train except that the flow rate through the high volume Modified Method 5 train is not specified. The smaller size of the Method 5 unit and the lack of a requirement for constant flow allows the train to be used for multipoint sampling.

In this method, the flue gas is sampled at representative points and at an isokinetic sampling rate (±10 percent). The result is that the particulate sample may be more representative of the flue gas than if the sample were taken at a single point of average velocity (SASS/Level 1 method). The other advantage of the high volume Modified Method 5 system is that the all glass system is useful where contamination or reactivity of substances from contact with stainless steel is suspected. However, no particulate size distribution data are attainable from high volume Method 5 sampling.

The design of the adsorbent column requires that this unit be operated in a vertical position with the resin packed tightly in such a way as to prevent channeling. The required detection capabilities of the analytical methods require that the system be designed to provide a sample of flue gas equivalent to that required for Level 2 testing (30 sm^3). The resin holder should likewise be designed to provide adequate capacity for the volume of gas sampled.

The high volume Modified Method 5 system should also follow the Level 1 guidelines for quality control and sample handling. An additional requirement of this system is that joints are glass to prevent contamination of the sample (no grease).

Midget Impinger Train

Formaldehyde is sampled with the midget impinger train. In the impingers, 2,4-dinitrophenylhydrazone is used to collect the formaldehyde by derivatization. Subsequent analysis is performed by HPLC or GC. Precise identification of formaldehyde can be achieved with GC/MS (62).

Evacuated Bag Sampling Train

The operation of the evacuated bag sampling train is described in EPA Methods 23, 110, and 106 (11,23,24,26). The schematic of this train is shown in Figure 11 in Section 5 of this report.

The EPA methods for gas sampling specify that the sampling probe be placed in the center of the stack and after leak checking and purging, the sample be collected at a sampling rate of 0.5 L/min. The collected gas sample is then available for analyses of vinyl chloride, vinylidene chloride, trichloroethylene, and benzene by on-site gas chromatography (GC).

Tube Sampling Train

The method proposed for sampling acrylonitrile is the NIOSH charcoal sampling tube procedure. The method can be integrated into the bag sampling train by installing two, three-way valves as shown in Figure 16. This arrangement minimizes equipment requirements (pumps, probes, etc.). The method also provides a backup method for benzene and vinyl chloride (NIOSH methods).

The NIOSH-type adsorbing tube contains two sections of activated charcoal, the first section containing 100 mg and the second section with 50 mg. The suggested sample volume is 10 liters with a sampling rate of 1 L/min. This method is limited by high temperature, high gas moisture content, and excessive sampling rates which decrease the adsorption capacity of the activated carbon. For flue gas streams, gas may need to be conditioned prior to collection.

LEVEL 2 FIELD STUDY

As an alternative to the previously described field study, a Level 2 field study for determining the thirteen suspect carcinogens was investigated. This program would be similar to the original field study except that the volatile organics would be sampled by a Tenax-GC sampling tube instead of a Tedlar bag train. This change does not reflect an accepted protocol and needs validation before such a field study could be conducted. The methods for this field study are summarized in Table 13. A schematic of the sampling system is shown in Figure 17.

The specific operating and handling methods for the sampling system have been discussed previously. The sections of this report on the analytical methods discuss the state-of-the-art technologies for analysis of these samples. The use of the Tenax-GC tube sampling train would preclude the option of on-site analysis by gas chromatography since desorption and analysis by gas chromatography/mass spectrometry (GC/MS) would be performed in the home laboratory. Since this method is not as subject to degradation as bag sampling, this change should not be a problem. The increased sensitivities and resolution of the GC/MS analysis would represent an improvement over the bag sample/gas chromatography analysis methods.

The proposed methods of sampling have a number of limitations which require a decision criteria for selection and operation. The choice of SASS train or high volume Modified Method 5 train is primarily dependent on the expected size distribution of the particulate emissions. In the "Methods and Procedures Manual for Sampling and Analysis" by Hamersma, *et al.*, a

TABLE 13. SUMMARY OF METHODS FOR LEVEL 2 FIELD STUDY

Compound	Collection matrix	Sampling method	Quantity of gas sampled	Analytical method	Interference
Asbestos	Particulate, filter	SASS/ HV-MM5	30 sm^3	STEM	Other fibers
Arsenic	Impinger (H_2O_2)	SASS/ HV-MM5	30 sm^3	Hydride generation AAS	
Beryllium	Particulate, filter	SASS/ HV-MM5	30 sm^3	AAS	
Cadmium	Particulate, filter	SASS/ HV-MM5	30 sm^3	AAS	
Nickel	Particulate, filter impinger	SASS/ HV-MM5	30 sm^3	AAS	
Dioxin	Particulate/ resin/ condensate	SASS/ HV-MM5	30 sm^3	GC/HRMS	
PAH	Particulate/ resin/ condensate	SASS/ HV-MM5	30 sm^3	GC/LRMS	
Trichloroethylene	Tenax-GC	Tube	10 liters	GC/LRMS	
Vinyl chloride	Tenax-GC	Tube	10 liters	GC/LRMS	
Vinylidene chloride	Tenax-GC	Tube	10 liters	GC/LRMS	
Benzene	Tenax-GC	Tube	25 liters	GC/LRMS	
Formaldehyde	DNPH/HCl	Midget impinger train			
Acrylonitrile	Charcoal	Tube	10 liters	GC/AFD	

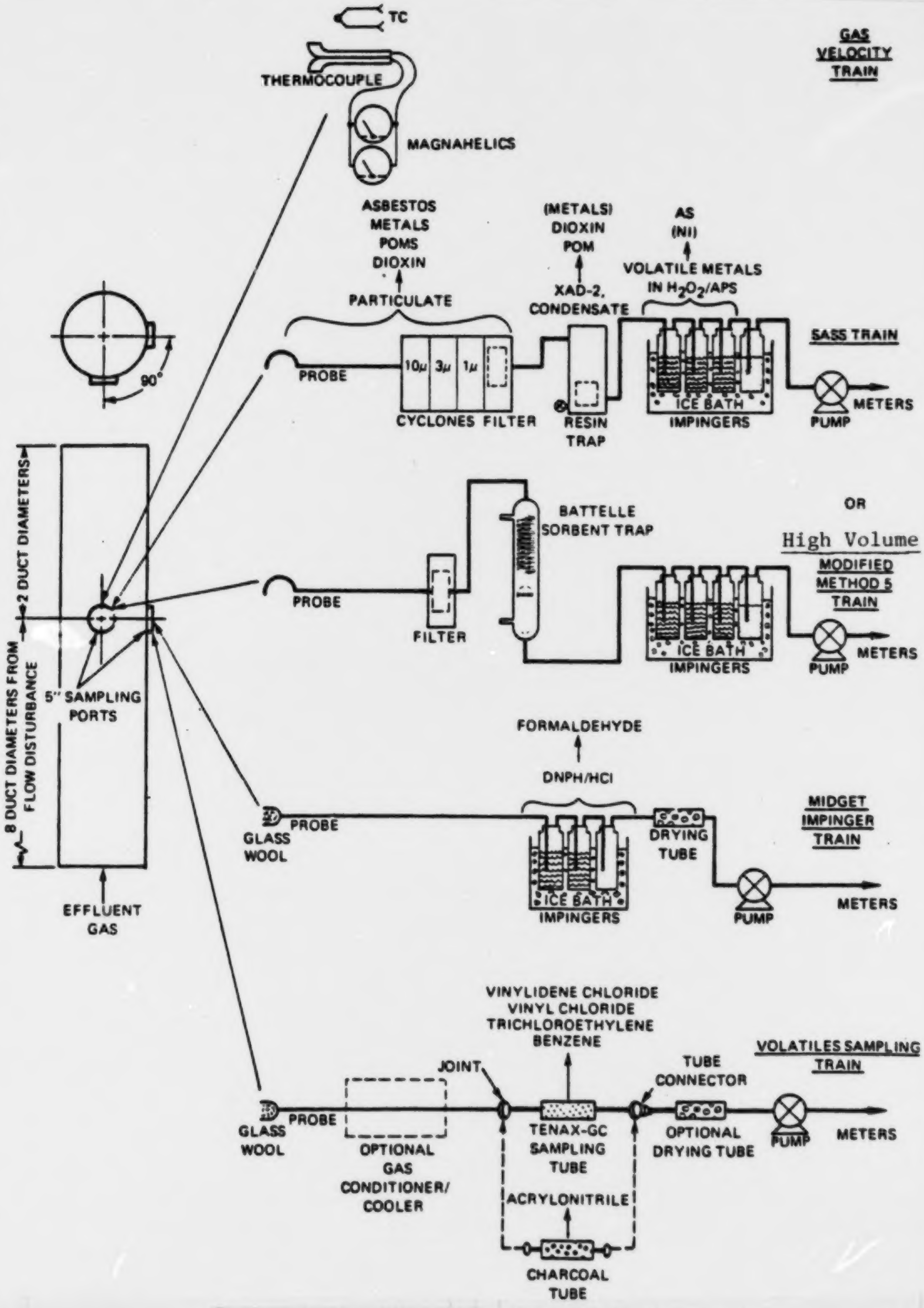
TC
THERMOCOUPLE
MAGNAHELICS
GAS VELOCITY TRAIN
ASBESTOS
METALS
POMS
DIOXIN
PARTICULATE
(METALS)
DIOXIN
POM
XAD-2,
CONDENSATE
AS
(NI)
VOLATILE METALS
IN H_2O_2/APS
SASS TRAIN
90°
PROBE
10μ
3μ
1μ
CYCLONES
FILTER
RESIN
TRAP
ICE BATH
IMPINGERS
PUMP
METERS
OR
BATTELLE
SORBENT TRAP
High Volume
MODIFIED
METHOD 5
TRAIN
PROBE
FILTER
ICE BATH
IMPINGERS
PUMP
METERS
8 DUCT DIAMETERS FROM
FLOW DISTURBANCE
2 DUCT DIAMETERS
5" SAMPLING
PORTS
EFFLUENT
GAS
FORMALDEHYDE
DNPH/HCl
MIDGET
IMPINGER
TRAIN
PROBE
GLASS
WOOL
DRYING
TUBE
ICE BATH
IMPINGERS
PUMP
METERS
VINYLIDENE CHLORIDE
VINYL CHLORIDE
TRICHLOROETHYLENE
BENZENE
VOLATILES SAMPLING
TRAIN
JOINT
TUBE
CONNECTOR
GLASS
WOOL
PROBE
OPTIONAL
GAS
CONDITIONER/
COOLER
TENAX-GC
SAMPLING
TUBE
OPTIONAL
DRYING TUBE
PUMP
METERS
ACRYLONITRILE
CHARCOAL
TUBE

Figure 17. Sampling system for Level 2 field study.

cutoff point of 5-10 mg of particulate catch per SASS cyclone was chosen for elimination of the cyclone (63). For source emissions with grain loading less than 0.02 gr/dscf, the catch in the >3 μm size range would be negligible. In these cases, the use of the high volume Modified Method 5 system would be recommended due to the ease of operation. For sources with known large particle-size distributions or for sources with high grain loadings, the use of the SASS train would be required to provide size fractionated particulate samples.

The operation of the volatiles sampling train is also subject to limitations. The size of the resin bed and the volume of gas sample require estimation of the potential source concentration. Particulate loading on the Tenax-GC sorbent can lead to sample line plugging and also sample loss by adsorption on carbonaceous particulate material. In sources with high grain loadings, the use of a prefilter and/or glass wool would be required. The effect of these filters on sample loss would require inclusion of these samples in the sample analysis system to determine the possibility of sample losses.

SECTION 8

COST MODEL

INTRODUCTION

The final task of these combined efforts as described in the Introduction of this report was to estimate the costs of determining the suspect carcinogens using the recommended sampling and analysis procedures. A cost estimate for each recommended procedure is given in Table 14. Incorporating multicomponent collection and quantification, the total cost for determining all twenty-one suspect carcinogens in a comprehensive field study would be $11,860. This figure, and those in Table 14, however, reflect only a per sample cost for a single analysis. In an actual field study, factors such as equipment, personnel, quality assurance, and travel are all major expenses. In this regard, a detailed cost model for the Level 2 field study with a SASS sampling train described in the previous section was developed and is presented here. It should be stressed that this model is based on 1981 dollars. Experience with inflationary pressures during recent years has shown that a model such as this estimate can show increases of at least 10 percent per year.

This model is given as an estimate derived from generalized cost elements. These calculations are at best within ±10 percent of the true costs for performing this type of study. An actual study, where field samples are taken, would require reviewing all cost elements for the expenses of that specific test program. Items such as travel cost from the home laboratory to the sampling site, special reports, special record requirements such as chain-of-custody, documentation, new Federal Register methodologies, mobile laboratory operations, and structural installations such as sampling platforms, are only a few of the additional cost elements that would affect the final cost.

This model is derived from establishing the labor, instrumentation, and laboratory capabilities and calculating the contribution of each of these cost elements as a function of time and materials contribution to each task. Thus, each operation associated with sampling and analysis was divided into its components and the cost of each suboperation was totaled to generate a combined estimate for all test costs. The main elements of cost which require careful definition are labor and direct instrument operation expenses.

LABOR ASSOCIATED COSTS

To perform a complex sampling and analysis test such as stack gas analysis for suspected carcinogens, a highly skilled mix of professional scientists is required. A cost basis for staffing requirements is shown in Table 15. The labor mix table also shows cost to the project on an hourly basis for each indicated labor category. This parameter is denoted Cost of Labor, COL, and the following equation shows the formula for calculating COL from the yearly compensation scheduled for each pay grade used.

$$\boxed{COL = [(S + F)(OH + B)] \div LHY}$$

TABLE 14. COST ESTIMATES FOR RECOMMENDED SAMPLING AND ANALYSIS PROCEDURES

Compound	Sampling method	Approximate cost ($)	Analytical finish	Approximate cost ($)	Overall sampling and analysis cost ($)
Acrylonitrile	Charcoal tube	100	GC/FID; 3% SP1000 on 100/120 mesh Supelcoport or GC/MS	100	200
Arsenic	Method 5 train/ Glass fiber filter; 0.1 *N* nitric impingers	500	Hydride generation AAS/ICP	40	540
Asbestos	Fluorocarbon membrane filter	100	Microscopic field counting	400	500
Benzene	Gas bulb/Tedlar bag	200	GC/FID; 0.1% SP1000 on 100/120 mesh Carbopak C	100	300
Beryllium	Method 5 train/ Glass fiber filter; 6 *N* nitric impingers (EPA Method 104)	500	Flame AAS/ICP	40	540
Cadmium	Method 5 train/ Glass fiber filter; 0.1 *N* nitric impingers	500	Flame AAS/ICP	40	540
Diethylnitrosamine	SASS train/Sorbent	500	GC/AFID; 3% SP2100 on 100/120 mesh Supelcoport	100	100
Dimethylnitrosamine	SASS train/Sorbent	500	GC/AFID; 3% SP2100 on 100/120 mesh Supelcoport	100	600
Dioxin	SASS train/Sorbent and filter catches	500	Ultrasonic extraction/GC/MS on AUE-HP packing	3,000	3,500
Ethylene dibromide	SASS train/Sorbent	500	GC/FID; 10% FFAP on 80/100 mesh Chrom WAW or GC/MS	100	600

TABLE 14. (Continued)

Compound	Sampling method	Approximate cost ($)	Analytical finish	Approximate cost ($)	Overall sampling and analysis cost ($)
Ethylene dichloride	Gas bulb/Tedlar bag	200	GC/ECD; 0.2% Carbowax 1500, 0.1% Carbopak C on 100/120 mesh Supelcoport	100	300
Ethylene oxide	Charcoal tube	100	GC/FID; Porapak QA	100	100
Formaldehyde	Impinger (DNPH) or Charcoal tube	200, 100	HPLC, Lichrosorb RP-18 or Ion Chromatography	100	100
Nickel	Method 5 train/ Glass fiber filter; 0.1 *N* nitric impingers	500	Flame AAS/ICP	40	540
Nitrosoethylurea	SASS train/Sorbent	500	HPLC: Thermal Energy Analyzer or UV	100	600
Nitrosomethylurea	SASS train/Sorbent	500	HPLC: Thermal Energy Analyzer or UV	100	600
Perchloroethylene	SASS train/Sorbent	500	GC/ECD; 0.2% Carbowax 1500, 0.1% Carbopak C on 100/120 mesh Supelcoport	100	600
PAH	SASS train/Sorbent and filter catches	500	GC/MS; 3% Dexsil 400 on 100/120 mesh Chrom WAW	500	1,000
Trichloroethylene, vinyl chloride, vinylidene chloride	Gas bulb/Tedlar bag field analysis	200	GC/FID	100	300

TABLE 15. COST BASIS FOR LABOR MIX

	Senior Technical Manager	Senior Engineer	Engineer/Chemist	Technician	Steno/Graphs
Equivalent Federal Pay Grade	GS-14, Step 7	GS-12, Step 7	GS-11, Step 5	GS-9, Step 3	GS-6, Step 3
Annual Compensation($)	45,443	32,339	25,486	19,825	14,584
Cost of Labor($)	65.32	46.49	36.64	28.50	20.96

where

S = base salary, civil service equivalent pay grade
F = fringe benefits, based on 30 percent of salary
OH = overhead rate, estimated at 130 percent of salaries and benefits
B = salary expense base, 100 percent of salary and fringes
LHY = hours in a person year, 2080 hours
COL = hourly cost of labor for a defined labor category.

Labor cost includes the fringe benefits paid for each employee estimated in this model as 30 percent of salary. Also, the overhead costs associated with operating the research facility are calculated in the model as a percentage of labor dollars. Operating overhead typically contains expenses such as support staff, facilities, furniture, facilities upkeep, building alterations, and repairs, research services such as data base, auditing, contracts staff, security, telephone, taxes, postal expenses, etc. The hourly labor rate is based on 2080 working hours or 52 weeks of 40 hours per week.

INSTRUMENT ASSOCIATED COSTS

The costs of operating research instrumentation fall into a special category because scientific instruments and complex sampling devices are subject to short lifetimes, high supplies cost, and high maintenance requirements. A model for instrument costs is shown in Table 16, where the elements of cost associated with operating several instruments and sampling devices are provided on a per hour basis.

For each instrument category, a verbal quote was secured from an instrument manufacturer who provided the current purchase price of each device. The instrument/sampler is amortized on a 5-year working lifetime without calculation of cost of capital to purchase the device through a loan or lease. Thus, for the purpose of this model, interest rate charges on capital are not considered.

If maintenance agreements were quoted by manufacturers, e.g., GC/MS systems, they were used to estimate maintenance costs; in other cases 10 percent of the purchase price was used to estimate maintenance costs. For the scanning transmission electron microscope, a lower estimate was used. Supply costs are estimated directly and utilities are estimated at 10 percent of the yearly cost element of purchase.

TABLE 16. ESTIMATED COST BASIS FOR YEARLY OPERATION OF SAMPLING EQUIPMENT AND ANALYTICAL INSTRUMENTATION($)

	Sampling Equipment			Analytical Instrumentation						
	SASS train	Modified Method 5 train	Volatiles sampling train	GC/HRMS	GC/LRMS	STEM	AAS	GC/FID	HPLC/UV	IC
Purchase Price (PP)*	29,016	10,096	8,961	400,000	150,000	384,000	34,000	25,000	20,000	30,000
Yearly Cost Element of Purchase (Amortized over 5 years)	5,803	2,019	1,792	80,000	30,000	76,800	6,800	5,000	4,000	6,000
Maintenance (12% of PP for GC/MS and STEM Systems, 10% of PP for other devices)	2,902	1,010	896	48,000	18,000	10,000	3,400	2,500	2,000	3,000
Supplies	1,000	1,000	1,000	15,000	15,000	5,000	3,000	3,000	4,000	3,000
Utilities (10% of yearly cost element of purchase)	580	202	179	8,000	3,000	7,680	680	500	400	600
Property Taxes**	836	291	258	11,520	4,320	11,059	979	720	576	864
Total Yearly Cost	11,121	4,522	4,125	162,520	70,320	110,539	14,859	11,720	10,976	13,464
Hourly Cost Based on 2080 Labor Hours	5.35	2.17	1.98	78.13	33.81	53.14	7.14	5.63	5.28	6.47
Utilization Factor***	90%	90%	80%	70%	60%	90%	80%	80%	80%	80%
Estimated Hourly Utilization Cost	5.94	2.42	2.48	111.62	56.35	59.05	8.93	7.04	6.60	8.09

*Obtained from appropriate companies.

**Based on a 10-year depreciation schedule, 72% average book value, at $40/1000.

***The fraction of estimated time the instrumentor train is available for sampling and analysis less required maintenance, calibration, retrofitting, and equilibration.

Utilities costs can be accurately estimated from the manufacturers' specifications for a specific model, but the figure used in this cost model gives representatives values. Some laboratory instruments require a high electrical load. A low resolution GC/MS, for example, may shed 20,000-30,000 Btu per hour as discharged heat which typically requires a peak load, 1-1/2 ton air conditioner to dissipate this excess heat. The power requirement for the air conditioner is an additional cost to the electricity demand of the instrument itself.

Property taxes are calculated as 4 percent of the instrument value based on a 10-year depreciation schedule. A 2080 hour work year is used to calculate hourly costs and an efficiency factor is applied to the hourly rate to reflect lost time due to routine maintenance, repair, and calibration. Some instruments such as the quadrupole GC/MS, used for low resolution mass spectrometry, exhibit significant "downtime" due to the frequent need to dismantle the instrument to clean internal parts, thus a 60 percent efficiency factor is used to calculate the time availability of this instrument for actual chemical analyses.

COMBINED COST MODEL

Once the labor and instrument costs are calculated, a combined cost model is generated by summing the costs of sampling, analysis, and data interpretation. The cost of performing analytical measurements for the thirteen suspect carcinogens is given in Table 17. The combined cost model for sampling and analysis based on a scenario of SASS train, formaldehyde impinger, and sorption tube sampling combined with Level 2 (GC/MS) analysis is illustrated in Table 18. Here the steps of sampling and analysis including planning, sample preparation, presite survey, sampling, sample delivery, engineering data evaluation, laboratory analyses, laboratory data evaluation, and reporting are incorporated into a cost matrix which includes labor, instrument, and supply related costs. From the summed matrix, the cost of sampling and analyzing thirteen suspect carcinogens is estimated to be $62,000.

TABLE 17. COST BASIS FOR LABORATORY ANALYSES—SASS SAMPLING WITH LEVEL 2 (GC/MS) ANALYSES

	Asbestos	Arsenic	Beryllium	Cadmium	Nickel	PAH Combined	Dioxin Workup	Acrylonitrile	Benzene	Formaldehyde	Trichloroethylene	Vinyl chloride	Vinylidene chloride
Resin, Collector/Solution													
Labor, Technician (hr)	-*	-	-	-	-	4	4	4	2	8	2	2	2
Sampling													
Labor, Technician (hr)	6	6	4	4	6	10	15	2	4	-	-	4	4
Supplies ($)	150	40	40	40	40	250	250	60	40	40	40	40	40
Analysis													
Calibration/QC Technician (hr)	4	2	2	2	2	20	10	4	2	2	2	2	2
Labor, Senior Chemist (hr)	24	2	2	2	2	40	30	4	2	2	2	2	2
Labor, Technician (hr)	-	8	6	6	8	-	-	-	-	-		-	-
Supplies ($)	20	30	30	30	30	50	50	10	10	10	10	10	10
Instrument Costs													
GC/HRMS (hr)	-	-	-	-	-	-	40	-	-	-	-	-	-
GC/LRMS (hr)	-	-	-	-	-	68	-	8	4	4	4	2	2
STEM (hr)	8	-	-	-	-	-	-	-	-	-	-	-	-
AAS (hr)	-	4	4	4	4	-	-	-	-	-	-	-	-
GC/FID (hr)	-	-	-	-	-	-	-	-	-	-	-	-	-
HPLC/UV (hr)	-	-	-	-	-	-	-	-	-	-	-	-	-
IC (hr)	-	-	-	-	-	-	-	-	-	-	-	-	-
Number of Subsamples	2	6	5	5	6	5	5	1	1	1	1	1	1

* (-) indicates no associated costs or labor

TABLE 18. COST MODEL SUMMARY FOR SAMPLING AND ANALYSIS OF SUSPECT CARCINOGENS IN STACK GAS EMISSIONS—(labor represents hours, other costs are given as 1981 dollars)

	Senior Manager (hr)	Senior Chemist (hr)	Engineer/ Chemist (hr)	Technician (hr)	Steno/ Graphics (hr)	Travel ($)	Subsistence ($)	Instrument Cost ($)	Shipping ($)	Supplies ($)	Totals ($)
Planning	24	-*	40	-	-	-	-	-	-	-	3,033
Preparation/ Calibration (Sampling)	-	-	32	80	-	-	-	-	-	-	3,452
Presite Survey	-	-	32	32	-	1,100	$240	-	-	-	3,424
Sampling	-	-	32	56	-	3,500	1,440	84	400	1,500	9,692
Sample Recovery/ Delivery	-	-	-	24	-	-	-	-	100	-	784
Data Processing (Engineering)	16	-	40	16	-	-	-	-	-	-	2,967
Sample Work-up and Analysis	-	116	-	177	-	-	-	10,264	-	1,370	22,071
Data Processing (Laboratory)	-	24	48	-	-	-	-	5,162	-	-	8,036
Technical Inputs/ Reporting	32	60	40	80	-	-	-	-	20	500	8,542
										TOTAL	$62,000

* (-) indicates no associated costs or labor.

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APPENDIX A

SAMPLING AND ANALYSIS PROCEDURES FOR ORGANIC SUSPECT CARCINOGENS

SAMPLING AND ANALYSIS PROCEDURES FOR ACRYLONITRILE

BACKGROUND

Acrylonitrile is a colorless liquid with the chemical and physical properties shown in Table A-1.

TABLE A-1. CHEMICAL AND PHYSICAL PROPERTIES OF ACRYLONITRILE

Property	Value
Formula	CH_2=CHCN
Molecular weight	53.03
Physical state	Liquid
Melting point	−84°C
Boiling point	77°C
Density	0.8060 (20°C)
Refractive index	1.3911
Solubility	Soluble in water, acetone, benzene, and alcohol

The principal production route to acrylonitrile is the SOHIO process which involves a high temperature catalytic reaction between propylene and ammonia.

SAMPLING AND ANALYSIS

Several sampling and analysis procedures have been used for acrylonitrile. Sampling has normally involved bubblers containing aqueous or organic solvent media or alternatively sorbent tubes using charcoal or porous polymer resins. Analysis has usually involved gas chromatography (GC) often followed by a selective detector such as a nitrogen-phosphorus detector or a mass spectrometer. Comparison of the relative benefits of these approaches is given in Table A-2.

Acrylonitrile was determined in air by Kugaczewska (1) by trapping it in aqueous solution and hydrolyzing with sodium hydroxide to give ammonia salts. The ammonia was then determined colorimetrically by reaction with sodium hypochlorite and sodium salicylate in the presence of sodium nitroferriccyanide. The sensitivity of the method was 0.5 mg/m^3 of air, but no information was given on the volume of air sampled.

Nazarona and Nakrap (2) used sulfanilic acid instead of benzidine. Air was sampled in H_2O bubblers at a rate of 15 L/min. Kondo sampled acrylonitrile in air by passing it through three bubblers in series containing pure water at 0°C (3). Flow rates were 0.5 L/min for 10 liter volumes of air. Samples were analyzed by gas chromatography on 1.5 percent PEG 6000 with 60/80 mesh Celite 545 as the support. The detection limit for acrylonitrile was 3.5 ppm.

TABLE A-2. ADVANTAGES AND DISADVANTAGES OF ACRYLONITRILE SAMPLING AND ANALYSIS PROCEDURES

Procedure	Advantages	Disadvantages
	Sampling	
Aqueous/organic solvent bubblers	Simple, inexpensive	Not much information available on recoveries
Tenax or other GC adsorbent or porous polymer	Thermally desorbed	Very low sampling volumes
Charcoal	High capacity	Poor recovery for low levels of analyte
	Analysis	
GC/FID	Simple, inexpensive	Not very specific, not sensitive to low quantities, many interferences expected
GC/NPD	High sensitivity, eliminates some interference	Not completely specific
GC/MS	Highly specific intermediate sensitivity	Expensive

Fasitta and Ticciardello (4) sampled acetonitrile and acrylonitrile by bubbling air through 35 percent aqueous methanol kept at -15°C. Analysis was by gas chromatography. Schultzl, *et al.* (5) evaluated several sampling techniques for hydrocarbon and odor constituents in air emissions and found Tedlar bags to be better than Mylar or Teflon. However, losses were observed for polar odorous species on standing.

Tedlar bags were also evaluated for acrylonitrile sampling by Penton (6). Fifty-liter bag samples were subsampled using charcoal adsorption tubes, eluted with methanol, and analyzed by GC using flame ionization detection (GC/FID). Results indicated that some acrylonitrile was lost on standing for periods as short as 4 hours. The minimum detectable quantity was 3 mg/m^3 for a 30-liter sample.

Several researchers have used charcoal adsorption tubes for trapping acrylonitrile. Sawicki (7) desorbed the charcoal with carbon disulfide for analysis by GC/FID. Gomez, *et al.* (8) determined acrylonitrile in workplace air by this method, and investigated the interferences in the method by the more common solvents. Marano, *et al.* (9) analyzed trace levels of acrylonitrile in complex matrices with this sampling method, but quantified it by GC using a nitrogen-phosphorus detector (NPD). Oomens (10) used a dual detector (FID-NPD) gas chromatograph for acrylonitrile analyses. Air samples (10 L) were concentrated on charcoal for analysis with a detection limit of 50 ppb. The standard NIOSH procedure (11) for acrylonitrile in air requires collection and concentration of acrylonitrile on charcoal tubes with analysis by gas chromatography. Charcoal tubes are eluted with methanol. For a twenty-liter air sample, the probable useful range was estimated to be between 4.5 and 135 mg/m^3, but lower concentrations could be measured provided the desorption efficiency is adequate. The recovery of low levels of acrylonitrile from charcoal adsorption tubes was investigated by Gagnum and Posner (12). These researchers found recovery levels lower than NIOSH method S-156 using 2 percent acetone in carbon disulfide as the desorbing liquid. Acrylonitrile was found to be stable on charcoal in the absence of inhibitor for periods greater than one week. Gas chromatography was used for quantification.

Sampling tubes filled with gas chromatography packing materials were used to concentrate organic pollutants in air by Russell (13). The tubes were thermally desorbed into a gas chromatograph and quantified using flame ionization and flame photometric detection. The breakthrough volume for acrylonitrile on Poropak N was found to be 3 to 5 liters of air at 100 mL/min and 25°C. The recommended sampling volume was 50 to 75 percent of breakthrough. Parsons and Mitzner (14) used tubes of Tenax-GC to collect air pollutants in ambient air and stack sources. The tubes were thermally desorbed and analyzed by gas chromatography. Trace organic analyses of pollutants in ambient atmospheres were performed using this same method by Brown and Purnell (15). Campbell and Moore (16) determined acrylonitrile, acrolein, acetonitrile, and acetone in workplace air using sampling tubes filled with Poropak N. Percent recoveries ranged from 86 to 105 percent for concentrations below 1 ppm.

Casper (17,18) used headspace gas chromatography for acrylonitrile analysis in air samples. Jacobs and Syrjola (19) applied a computerized infrared analyzer to monitor acrylonitrile in air in the presence of other components without prior separation. Syrjola (20) used a Model 80 Gas Analyzer to monitor atmospheric pollutants. The microcomputer controlled single beam infrared analyzer could analyze up to eleven compounds with the appropriate interference corrections. Gas chromatography/mass spectrometry was used by Satoh (21) to identify organic compounds and determine acrylonitrile. Air from the Kawasaki industrial area in Japan was trapped and concentrated in liquid oxygen traps at sites around the plants. Koosker (22) discussed methods to determine various organic gases in the atmosphere and recommended the combination of glass capillary column chromatography/mass spectrometry for trace measurements.

The EPA/RTP-IERL Level 2 Analysis Manual (23) recommends GC/MS for nitriles, but no information was given on preferred sampling methods. Chromatography was accomplished using 3 percent SP 1000 on a 100/120 Supelcoport column.

DISCUSSION/RECOMMENDATIONS

Based on the results of this literature survey, the method of choice for acrylonitrile is gas chromatography. The major differences between the various methods are in sample collection and preconcentration, and the choice of detector used for quantification.

The need to concentrate samples is determined by the concentration of the acrylonitrile in the sample, and by the detection limit of the particular instrumentation chosen for quantification. Because of the scarcity of information on acrylonitrile emissions in stack gases, it must be assumed that the levels are low and provisions must be built into the method for the determination of low levels of analyte.

Sampling

Although several researchers have used aqueous or aqueous/organic solvent mixtures in bubblers or impingers for sampling acrylonitrile, the most widely reported trapping methods are those employing solid adsorbent tubes of charcoal, Tenax, or other porous polymers, such as those used for gas chromatographic supports (e.g., Poropak N). Of these solid adsorbents, Tenax-GC has received the most attention and is used most often. However, the data presented in the various publications surveyed in this review indicate that the retention characteristics of acrylonitrile on Tenax are such that the safe sampling volumes would be quite small. The safe sampling volume per gram of Tenax is approximately 3 liters of air per gram of Tenax for flow rate of 5 to 200 mL/min at 25°C. Because of the small sample, the concentration factor would also be very small.

Other porous polymers are not expected to perform more efficiently and the data are also scarce although, for Poropak N, the breakthrough volume was reported and found to be 3 to 5 liters of air at 100 mL/min at 25°C. The maximum recommended sampling volume for this sorbent was estimated to be 50 to 75 percent of the breakthrough volume, or 1.5 to 2.5 liters. With such small concentrations, the sensitivity of the measurement technique becomes very important.

Most sampling of air and emissions for acrylonitrile analysis is done using charcoal. The adsorptive capacity of charcoal for acrylonitrile is on the order of 4 percent by weight according to one report (NIOSH method), but this can vary depending upon the characteristics of the adsorbent. The main problem with charcoal adsorption tubes is the possibility of losses of very low levels of analyte upon desorption with organic solvents.

A recent investigation of recoveries of acrylonitrile from charcoal concluded that acrylonitrile could be recovered (>90 percent) with good precision from charcoal at the level of 16 μg per 100 mg charcoal (12) by using a mixture of acetone and carbon disulfide rather than methanol for desorption. This amount corresponds to vapor levels of 0.5 ppm for a 15-liter air sample. Below the 16 μg/100 mg charcoal level, recoveries were generally less than 90 percent for vapor phase application of acrylonitrile.

Because of expected low recoveries of acrylonitrile on charcoal, large sampling volumes would be required to achieve lower detection limits, but at the same time backup sections of charcoal adsorbent would be required should the levels be higher than expected.

Methods of Detection

The three possible choices of detectors for GC separation of acrylonitrile are flame ionization detection, nitrogen specific detection, and low or high resolution mass spectrometry with or without selected ion monitoring.

Flame ionization detection could only be used with relatively high levels of acrylonitrile. The most logical choice, based upon cost and ease of use, is nitrogen specific detection with an alkali flame detector (AFD), a thermionic specific detector (TSD), or nitrogen specific phosphorus detector (NPD). The use of this type of detector would reduce background interferences encountered with the FID and increase sensitivity. One publication estimated the detection limit of the nitrogen specific detector at 10 picograms (9). The use of high resolution mass spectrometry with selected ion monitoring would, of course, be the preferred detection technique, but the increased cost would be prohibitive in some cases.

RECOMMENDED PROCEDURES

- Charcoal adsorption with 100 to 500 liter volumes sampled.
- Charcoal desorption with methanol or mixture of methanol and acetone (cannot use CS_2 with NPD).
- Separation and quantification with GC/NPD. (GC/MS-SIM for qualitative identification and quantification).

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SAMPLING AND ANALYSIS PROCEDURES FOR BENZENE

BACKGROUND

Benzene is a volatile, colorless, and flammable liquid aromatic hydrocarbon that possesses a gasoline-like odor (1,2). The physical properties of benzene are shown in Table A-3. Benzene is used primarily as a chemical raw material in the synthesis of styrene, polystyrene plastics, and synthetic rubber; phenol and phenolic resins; cyclohexane and nylon; aniline; maleic anhydride, polyester resins, alkylbenzenes, and detergents; chlorobenzenes and materials used in the production of drugs, dyes, insecticides, plastics, and solvents. Benzene is a major component of gasoline.

TABLE A-3. CHEMICAL AND PHYSICAL PROPERTIES OF BENZENE

Property	Value
Formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Melting point	5.5°C
Boiling point	80.1°C
Density	0.878 (20°C)
Refractive index	1.5011
Solubility	Soluble in alcohol and acetone; low solubility in water (0.18 g/100 g H_2O at 25°C)

Benzene is manufactured from petroleum, e.g., reforming separation, platforming, dealkylation, transalkylation, pyrolysis of gasoline, and from coal and coal tar (1). Approximately 11 billion pounds of benzene were produced in the United States in 1976 (3). Of this total, an estimated 260 million pounds may have been emitted to the air (3). The principal sources of benzene emissions are chemical manufacturing facilities, petroleum refineries, gasoline storage and handling facilities, coke ovens, and automobiles (3). U.S. production of benzene in 1979 was approximately 11.8 billion pounds (4).

Benzene undergoes three distinct types of reactions: addition, cleavage, and substitution, the last being the most important (1). Halogenation, nitration, sulfonation, and alkylation lead to mono- and higher substituted products (isomers) with the ratio of the latter being roughly a function of the dipole moment of the molecule (1,2). Benzene also undergoes such reactions as chloromethylation, mercuration, and Friedel-Crafts acylation (1).

Under controlled catalytic oxidation, benzene can be oxidized to benzoquinone, maleic anhydride, and phenol (1). Rigorous chemical oxidation converts benzene to water and carbon dioxide. Benzene can be reduced catalytically to cyclohexane. Pyrolysis converts this compound to biphenyl, carbon, and hydrogen (1,2).

Photolytic studies indicate that no appreciable amounts of light at wavelengths longer than 280 nm (2800 Å) were directly absorbed by benzene dissolved in cyclohexane (2). Photolysis of benzene by light with a wavelength of less than 290 nm in the vapor phase and in oxygenated aqueous solution yields 2-formyl pyran and cyclopentadiene-carboxaldehyde (2). Atomic oxygen generated from the photodecomposition of nitrogen dioxide is known to react with benzene in a smog environment (2).

Benzene is very flammable, volatile, and toxic and must be handled with great caution. The storage, shipping, and labeling of benzene are therefore heavily regulated by OSHA, EPA, DOT, the CPSC, and NIOSH. New regulations are published in the *Federal Register* and all regulations are compiled annually in the Code of Federal Regulations (CFR). DOT regulations governing the interstate transportation of benzene are compiled in Volumes 14, 46, and 49 of CFR. Benzene in consumer goods is regulated by the CPSC, Volume 21 CFR. OSHA regulations are contained in Parts 1501, 1502, and 1503 of Volume 20. A permanent standard for the regulation of benzene appears in Part 1910 of the *Federal Register*, 43 (29), February 10, 1978. NIOSH recommends adherence to the present Federal standard of 10 ppm as a time-weighted average for worker exposure with a ceiling of 25 ppm (but without the permitted excursion to 50 ppm as in the existing standard).

SAMPLING AND ANALYSIS

Knoll, *et al.* (5) tested the use of Tedlar bags to contain gaseous benzene samples at source concentrations. Sample stability over time typically required in field studies, preuse effects, decontamination procedures, and the temperature range over which the bags can be successfully used were subjects of this study. Benzene samples remained essentially unchanged for up to 17 days. Cooling to −40°C or heating to 70°C did not produce concentration changes. Above 105°C decomposition of the bag seals was observed. No evidence of permeation loss at room temperature was observed, and absorptive loss could be observed only on prolonged contact. Flushing the bags with nitrogen was sufficient to remove all traces of previous samples. Calibration mixtures were prepared in Tedlar bags by injecting measured quantities of liquid benzene into a volatilization chamber leading to the bag while metering in nitrogen gas. These bag standards were used to perform calibrations for the GC measurement of benzene containing cylinders.

Knoll, *et al.* (5) have proposed a method for the determination of benzene from stationary sources. In this method, an integrated bag sample of stack gas containing benzene and other organics is analyzed by gas chromatography (GC), using a flame ionization detector (FID). The method is not applicable where the benzene is collected on particulate matter. The bag sampling used is shown in Figure A-1. The procedure is applicable to the measurement of benzene in the 0.1 to 70 ppm range. The upper limit may be extended by extending the calibration range or by diluting the sample. Although the chromatographic columns and the corresponding operating parameters described have been represented as being useful for producing an adequate resolution of benzene, interferences may be encountered with some sources. Adequate resolution is defined as an area overlap of not more than 10 percent of the benzene peak.

Gas mixture standards consist of gas cylinders of 5 and 10 ppm benzene in nitrogen for which the gas composition has been certified with an accuracy of ±3 percent or better by the manufacturer. The manufacturer must recommend a maximum shelf life for each cylinder so

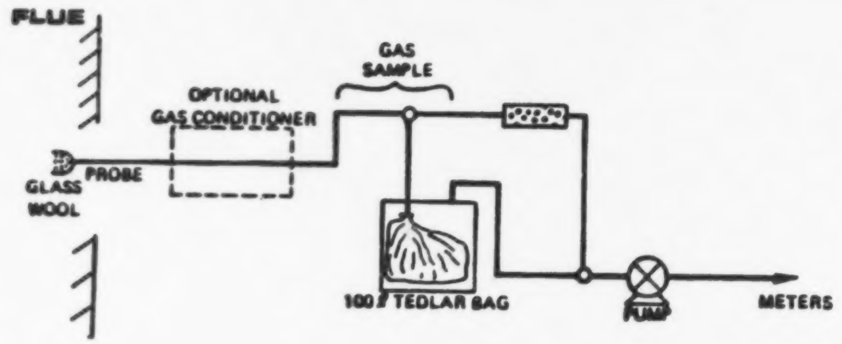

Figure A-1. Schematic diagram of grab sampling method for volatile organic species.

that the concentration does not change by greater than ±5 percent from the certified value. The concentration of benzene in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis using an analytical procedure that the manufacturer had calibrated on the day of cylinder preparation.

The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent: (1) verification value by comparison with a gas mixture using 99 mole percent benzene, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards.

A sampling and analysis method for benzene in air employing adsorption on charcoal, followed by desorption and gas chromatography has been described (6). The atmospheric sampling train consists of a charcoal tube, a vacuum pump, and a flow meter. A personal sampler pump or a dependable hand pump may be calibrated to produce the desired air volume. A known volume of air is drawn through a charcoal tube to trap the organic vapors present. The charcoal in the tube is transferred to a small test tube and desorbed with carbon disulfide and an aliquot of the desorbed sample is injected into a gas chromatograph for analysis.

The lower limit of detection for benzene with instrument attenuation and splitter techniques is 0.01 mg for each sample. This value can be lowered by reducing the attenuation or by eliminating the splitter. The upper limit value for benzene is 6.0 mg/sample. This value is the number of milligrams of benzene which the front section will collect before a significant amount passes to the backup section. Interferents are water present as a mist and any compound with the same retention time in the gas chromatograph as benzene. The accuracy and precision with benzene are shown in Table A-4. One disadvantage of the method is that the amount of sample that can be obtained is limited by the amount of benzene that the tube will hold before overloading as indicated by benzene recovery at the tube outlet. Also, the precision is limited by the reproducibility of the pressure drop across the tube, which affects the flow rate.

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TABLE A-4. PRECISION AND ACCURACY OF BENZENE ANALYSIS

	Accuracy	Precision
Motor driven laboratory pump	7.6%	4.2%
Approved coal mine personal sampling pump (calibrated with no in-line resistance)	13.6%	10.1%
Approved coal mine personal sampling pump (calibrated with charcoal tube in line)	8.8%	11.6%

Methods for the determination of exposure to benzene include gas detector tubes and portable instruments. Gas detector tubes contain a chemically impregnated packing that indicates the concentration of contaminant in the air by a chemically produced color change. The color changes are not permanent or stable, so the stained tubes must be read immediately after the samples are taken. The length of stain or the color intensity is read and compared with a control chart, e.g., a color comparator or a direct concentration reading from calibration works on the tube. Certification standards require that certified tubes have a range 1/2 to 5 times the time-weighted average concentration.

Brown and Purnell (7) investigated the adsorption characteristics of Tenax-GC, a polymer of 2,6-diphenyl-p-phenylene oxide for benzene. The main advantages of this material over other porous polymers are high temperature stability, low bleed thermal desorption, and a relative insensitivity to the effects of water vapor. For benzene sampled on a Tenax tube under the parameters listed in Table A-5, a retention volume of 8 L was measured at 20°C. A safe handling volume of 4 L, and a safe sampling volume/gram of adsorbent of 31 L were derived for benzene on Tenax-GC of these conditions.

Fentiman, *et al.* (8) measured benzene in the vicinity of users, producers, and dispensers of benzene products. Air samples were collected by pulling air through a bed of Tenax-GC for

TABLE A-5. OBSERVED SAMPLING AND THERMAL DESORPTION PARAMETERS FOR BENZENE ON TENAX-GC

Tenax sample	0.13 g
Flow rate	5–600 mL/min
Vapor concentration	<250 mg/m^3
Desorption temperature	100°C
Temperature	≤ 20°C

8 hours at 40°C and a flow rate of 30 mL/min. For analyses, the benzene was desorbed from the Tenax with a 10 mL/min stream of helium for 10 minutes and collected on the head of a GC column by means of a dual valving arrangement utilizing two 8-part valves.

DISCUSSION/RECOMMENDATIONS

EPA Method 110 employing Tedlar bags for the collection of benzene and other organics, followed by gas chromatographic analysis, using a flame ionization detector is recommended for the determination of benzene from stationary sources. The method is applicable to the measurement of benzene in stack gases only from specified processes; it is not applicable where the benzene is condensed or entrained with particulate matter. The procedure is applicable to the measurement of benzene in the 0.1 to 7 ppm range and the upper limit may be extended by extending the calibration range or by dilution of the sample. In these bags, benzene samples remained essentially unchanged where held at ambient temperatures for up to 17 days, when cooled to -40°C for one hour, or when heated to 70°C for one hour. At room temperature, no evidence of permeation loss was noted and absorptive loss could only be observed upon prolonged contact. Flushing the bags three times with nitrogen was sufficient to remove all traces of previous samples.

Resolution interferences which may be encountered on some sample sources may be eliminated by selecting a column which is best suited to the particular analysis problem. Column choices might include a stainless steel 2.44 m × 3.2 mm column containing 10% (W/W) TCEP on 80/100 mesh Chromosorb P-AW for the determination of benzene in the presence of aliphatics or a stainless steel 1.83 m × 3.2 mm column containing 5% SP 1200/1.75% Bentone 34 on 100/120 mesh Supelcoport for the determination of benzene with separation of xylene isomers.

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SAMPLING AND ANALYSES PROCEDURES FOR 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN

BACKGROUND

Chlorinated dibenzodioxins and dibenzofurans have been found as contaminants in fungicides (pentachlorophenol), herbicides (2,4,5-T), polychlorinated biphenyls (PCBs), and products from commercial processes in which polychlorinated phenols are used (animal fats and tallows) (1). Emissions of polychlorinated dibenzo-p-dioxins, dibenzofurans, and PCBs from combustion sources have been reported in recent studies (1). The analysis of these emissions indicates the presence of the extremely toxic 2,3,7,8-isomer of tetrachlorodibenzo-p-dioxin (TCDD) in some of the samples (1).

The physical and chemical properties of 2,3,7,8-TCDD are listed in Table A-6 (2). The low solubility and vapor pressure of 2,3,7,8-TCDD suggest the potential to adsorb and remain on solid surfaces with which the TCDD comes in contact. Bioaccumulation would be anticipated because of selective solubility in organic liquids. The thermal stability of 2,3,7,8-TCDD in air (up to a temperature of 700°C) suggests that this dioxin will be persistent (2).

TABLE A-6. CHEMICAL AND PHYSICAL PROPERTIES OF 2,3,7,8-TCDD

Property	Value
Formula	$C_{12}H_4Cl_4O_2$
Molecular weight	322
Physical state	Solid
Melting point	303°C
Boiling point	—
Density	—
Refractive index	—
Solubility	Low in water (.0002 mg/L) and benzene (5 mg/L)
Vapor pressure	10^{-6}–10^{-7} mm Hg

Harris, *et al.* (2) reported a photolysis half-life for 2,3,7,8-TCDD in the gas phase under environmental sunlight conditions on the order of 5 to 24 days. These investigators also suggested that oxidation of 2,3,7,8-TCDD by the hydroxyl radical in the atmosphere would also be rapid. Handling precautions for TCDD are warranted because of reports of human symptoms resulting from acute high concentration exposure dating back to 1949 (2). Observed early symptoms demonstrate the irritating nature of this chemical (eye, respiratory tract). A variety of pathological conditions develop after a short latent period, including chloracne, porphyria cutanea tarda, severe muscle pain, hyperpigmentation, psychopathological effects, severe muscle pain, high blood lipids, and gastrointestinal problems (2). Specific instances of acute high concentration exposure at several industrial chemical plants raise the suspicion of increased risk of neoplasia; however, the data are preliminary (2). The results from chronic lower level exposures do not assure that exposure to less than 1 ppm is safe (2). Carcinogenesis studies on 2,3,7,8-TCDD using mice and rats have led to results which have caused regulatory agencies to list the compound as a carcinogen or suspected carcinogen (2). Harless, *et al.* (3) emphasize the grave health hazards of 2,3,7,8-TCDD if handled improperly. They suggest that techniques used for handling radioactive and infectious materials should be used by laboratory workers studying 2,3,7,8-TCDD. Only qualified individuals who are trained in laboratory procedures and are familiar with the hazards of 2,3,7,8-TCDD should handle this substance. Females of childbearing age should not handle 2,3,7,8-TCDD. According to Harless, *et al.* (3) a good laboratory practice involves routine physical examinations and blood checks of employees working with this compound. Also, facial photographs using oblique photoflood lighting should be periodically taken to detect chloracne, an early indicator of exposure to 2,3,7,8-TCDD (3).

SAMPLING AND ANALYSIS

Harless, *et al.* (3) investigated the analytical extraction, clean-up procedures, and capillary column gas chromatography/high resolution mass spectrometry methods for determination of 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). The application of these procedures and methods in the analysis of human milk, beef liver, fish, water, and sediment is described. The 2,3,7,8-TCDD methodology provided a mean percent recovery of 80 percent for 2.5 to 10 ng of $^{37}Cl_4$-2,3,7,8-TCDD internal standard, and a mean percent accuracy of ± 23 percent for 1 to 1250 pg in quality assurance samples. The precision of the gas chromatography/high resolution mass spectrometry method was determined to be ±20 percent relative to 2 to 10 pg 2,3,7,8-TCDD quantification standards during daily operations (3).

Buser and Bosshardt (4) identified TCDD isomers in methylene chloride extracts of fly ash (5-10 g). After centrifugation, the combined extracts were evaporated and purified on a silica microcolumn (0.5μ silica, 70-230 mesh, Merck, in 150 × 5 mm disposable Pasteur pipettes) eluting with 5 mL of hexane. Chromatography was carried out on an alumina-microcolumn (1.0 g alumina, basic, Woelm) using 10 mL portions of 2 percent and 50 percent methylene chloride in n-hexane. GC/MS analysis of the concentrated polychlorinated dibenzodioxin (PCDD) fraction indicated that more than 30 individual PCDDs can be identified in fly ash from municipal incinerators and industrial furnaces. However, the known highly toxic PCDD-isomers are only minor constituents (4).

Eiceman, *et al.* (5) analyzed fly ash samples collected from municipal incinerators in Japan, Canada, and the Netherlands. Samples were extracted for 12 hours in a Soxhlet apparatus with 200 mL of benzene. The extract was concentrated to 100 μL and analyzed by GC and GC/MS, including selected ion monitoring. Mass spectra were used to identify approximately 100 organic compounds, including polychlorinated dibenzofurans, polychlorinated dibenzo-p-dioxins, polychlorinated benzenes, polychlorinated phenols, polycyclic aromatic hydrocarbons, phthalate esters, and aliphatic hydrocarbons. Estimated concentrations of total organic mass extracted were 1 to 30 μg/g. Polycyclic aromatic hydrocarbons were present at 1 to 500 μg/g of fly ash; the sum of TCDD isomers was an estimated 2 to 10 ng/g (5).

Eiceman, *et al.* (6) also solvent extracted PCDDs and other organic compounds from 10 to 20 g samples of fly ash from municipal incinerators with 200 mL of benzene using ultrasonic agitation for one hour. Extracts were concentrated to 100 mL using a rotatory evaporator and analyzed directly by gas chromatography/mass spectrometry including selected ion monitoring for PCDDs. Results from five replicate analyses of a fly ash sample yielded averages and standard deviations (ng/g) for the tetra- to octa-chlorinated dibenzodioxins of 8.6 ± 2.2, 15.0 ± 4.0, 13.0 ± 3.4, 3.2 ± 1.0, and 0.4 ± 1, respectively (6).

Johnson (7) states that the predominant method for dioxin source sampling employs a filter followed by a solid sorbent material. Any standardized EPA stack sampling method for dioxins should be based on the sorbent approach. Particulate associated dioxin is caught by the filter while the sorbent collects vapor phase dioxin. The source assessment sampling system (SASS) is a high-volume (5 cfm) train, while the Modified Method 5 train is a conceptually identical but lower volume (1/2-1 cfm with sorbent in place) organic sampling system. Diagrams of a SASS, a Modified Method 5 train, and a sorbent train have already been shown. The ability of the SASS to provide a large sample to the analyst will dictate the use of this train (7). When sufficient sample is not a problem, the smaller and more corrosion-resistant Modified Method 5 train may be the proper choice. Most samplers employ XAD-2 resin as the sorbent material. Polyurethane foam is often used as the sorbent for sampling ambient air for dioxins and polychlorinated biphenyls but it is not a serious candidate for stack sampling. Table A-7 shows the trains selected for dioxin sampling by several organizations (7).

TABLE A-7. DIOXIN SAMPLING TRAINS OF SELECTED ORGANIZATIONS

Organization	Train used	Sorbent or solvent
EPA-IERL-RTP	SASS MM5*	XAD-2
EPA-ESRL	MM5	XAD-2
EPA-Region VI	MM5	XAD-2
EPA-Proposed test Plan (7/80) for Hempstead, N.Y.	SASS	XAD-2
USAF	Solvent-filled impinger	Benzene
DOW	Method 5	None

*Modified Method 5

One common variation in the sorbent sampling train is the presence or absence of a filter. Either a filter or impingers must be included to prevent plugging of the sorbent bed by particulate material. The particulate and sorbent catch both must be analyzed since dioxin may be found in both train elements.

The most widely used sample preparation for TCDD analyses for fish, fat, or meat involves sample extraction with ethanol and aqueous potassium hydroxide refluxing (2). The resulting solution is then extracted with benzene/hexane solvent. The organic phase is washed with concentrated sulfuric acid, filtered through a drying agent, and concentrated. A similar extraction procedure involves separate shake-extractions with methylene chloride, sodium hydroxide, sulfuric acid, and water. The extract is then passed through a drying column and concentrated by means of a hexane solvent-exchange procedure (8). Figure A-2 shows a schematic diagram of this clean-up procedure.

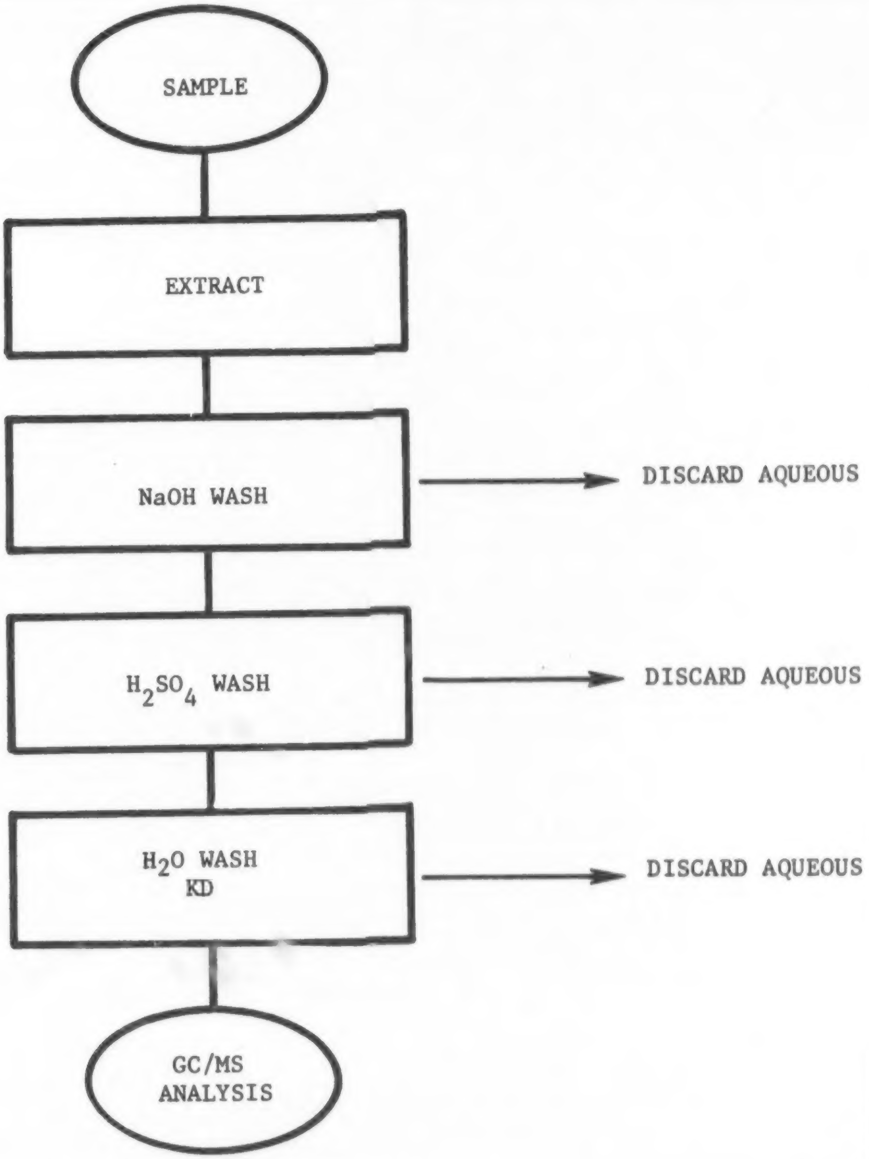
SAMPLE
EXTRACT
NaOH WASH
DISCARD AQUEOUS
H2SO4 WASH
DISCARD AQUEOUS
H2O WASH
KD
DISCARD AQUEOUS
GC/MS
ANALYSIS

Figure A-2. Schematic diagram of TCDD clean-up procedure.

Although the preceding extraction procedures are effective in separating TCDD from the sample matrix, several common environmental contaminants, i.e., DDE, DDT, and PCBs, will be extracted along with TCDD. These interferents are removed by column chromatography (2). A reported column packing is alumina (two columns) with hexane, carbon tetrachloride, and methylene chloride as the eluants. Combined gas chromatography/mass spectrometry (GC/MS) is the method of choice for the analysis of TCDD (2). This technique has the sensitivity and specificity to determine TCDD in the part per trillion range if there has been suitable sample preparation. Capillary column GC in which the GC phase is coated onto the wall of a long, narrow diameter column is being extensively used for TCDD determinations. For a determination of total chlorinated dioxins in a sample either LRMS or HRMS may be used. The difference between the two is primarily one of mass measurement accuracy (2). For a specific 2,3,7,8-TCDD determination, capillary column GC with HRMS is necessary to separate the 2,3,7,8-isomer from other isomers and to ensure that the sample does not show any interferences (2). Figure A-3 shows a schematic diagram of a proposed TCDD screening and analysis procedure (8).

Shih, *et al.* (9) describe ambient air sampling for TCDD with a sampling train consisting of four Greenberg-Smith impingers, the first two with frits and filled with benzene, the third and fourth without frits and filled with activated carbon to absorb benzene vapors (Figure A-4). The pump was operated at 1 L/min and samples ranged from 180 to 300 liters.

As described by Shih, *et al.* (9), U.S. Air Force stocks of Herbicide Orange were burned at sea and samples of the combustion gases collected by (a) a USAF benzene impinger train and (b) a Lear-Siegler Method 5 train modified with an organic vapor sorbent trap containing XAD-2 (Figure A-5).

Dow Chemical Company used a RAC Staksampler, Method 5 train to collect particulate and vapor samples from the stacks of Dow Midland's tar burners and rotary/kiln incinerators and a power plant (9). PCDDs were found in these samples.

Reported analyses in the low parts per trillion region suggest that background interferences are of major importance in TCDD analyses. Thus, the sample must be extracted and sufficiently cleaned to either eliminate or at least minimize any interfering components. 2,3,7,8-TCDD is normally found associated with a variety of compounds which interfere with analysis. For example, polychlorinated biphenyls (PCBs) are often found in sample matrices along with 2,3,7,8-TCDD. Since their complete separation from 2,3,7,8-TCDD by chromatographic means is difficult, they can either mask low levels of 2,3,7,8-TCDD or contribute to the apparent 2,3,7,8-TCDD level. The problem is not solved by low resolution mass spectrometry. Fragment ions from various PCBs can contribute to the ion current at m/e 320 and m/e 322, two mass-to-charge ratios commonly monitored for the determination of 2,3,7,8-TCDD. As an example, heptachlorinated biphenyl exhibits ion current at m/e 322 and m/e 324 by loss of two chlorine radicals from its molecular ion. Dehydrochlorinated DDT presents a similar problem. As a result, accurate 2,3,7,8-TCDD determination can only be made if the interfering species are removed or if a TCDD-selective measurement is performed.

Many different extraction-cleanup methods have been proposed (10-20). The first category involves a basic pH extraction step whereas the second category utilizes only neutral extraction conditions. The neutral extraction technique (18,21) was developed on the possibility that treatment with strong base might generate compounds which could form chlorinated dioxins in the mass spectrometer (19). The subsequent cleanup steps are similar for

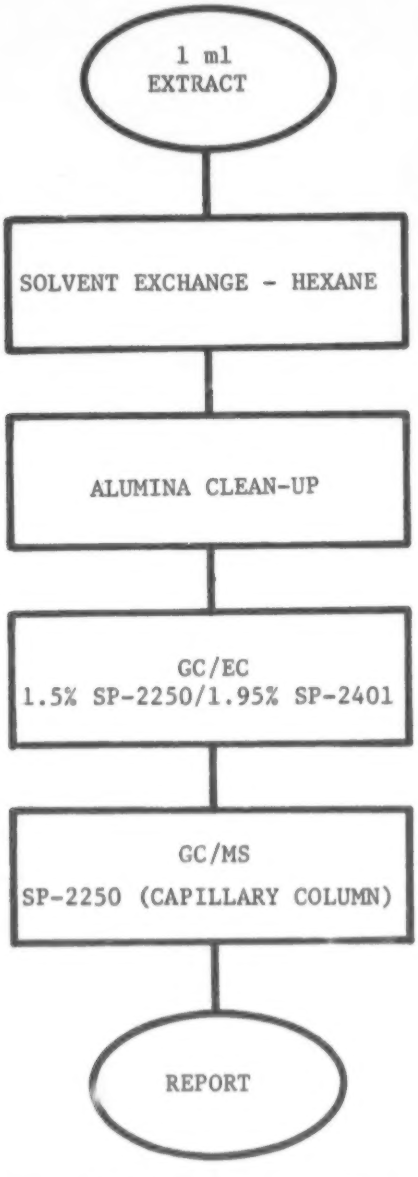
1 ml
EXTRACT
SOLVENT EXCHANGE - HEXANE
ALUMINA CLEAN-UP
GC/EC
1.5% SP-2250/1.95% SP-2401
GC/MS
SP-2250 (CAPILLARY COLUMN)
REPORT

Figure A-3. Schematic diagram of TCDD screening and analysis procecure.

the two techniques and differ only in the application and complexity of the procedures. Both of these extractions are described in detail below.

Base Extraction Method

A typical basic extraction-cleanup technique consists of heating ten grams of solid sample with 10 mL of ethanol and 20 mL of 40 percent potassium hydroxide solution for thirty minutes (20). After cooling, an additional 10 mL of ethanol is added and the solution is extracted with four 10 mL portions of hexane. The cleanup procedure consists of washing the combined

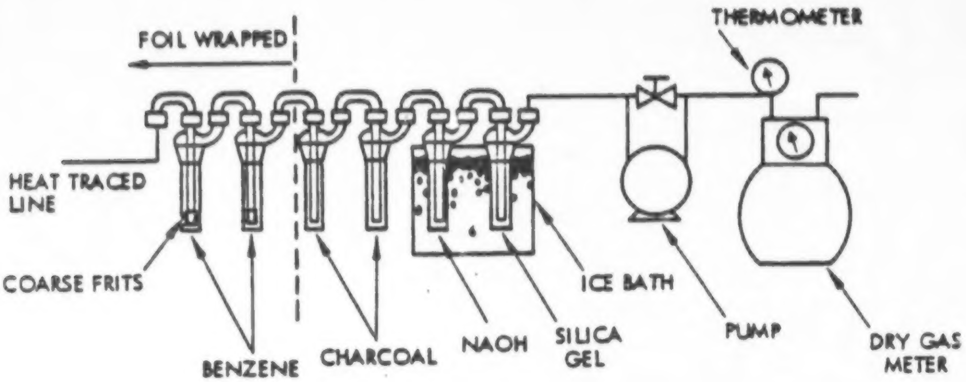
FOIL WRAPPED
THERMOMETER
HEAT TRACED LINE
COARSE FRITS
BENZENE
CHARCOAL
NAOH
SILICA GEL
ICE BATH
PUMP
DRY GAS METER

Figure A-4. USAF benzene impinger train used for herbicide orange testing.

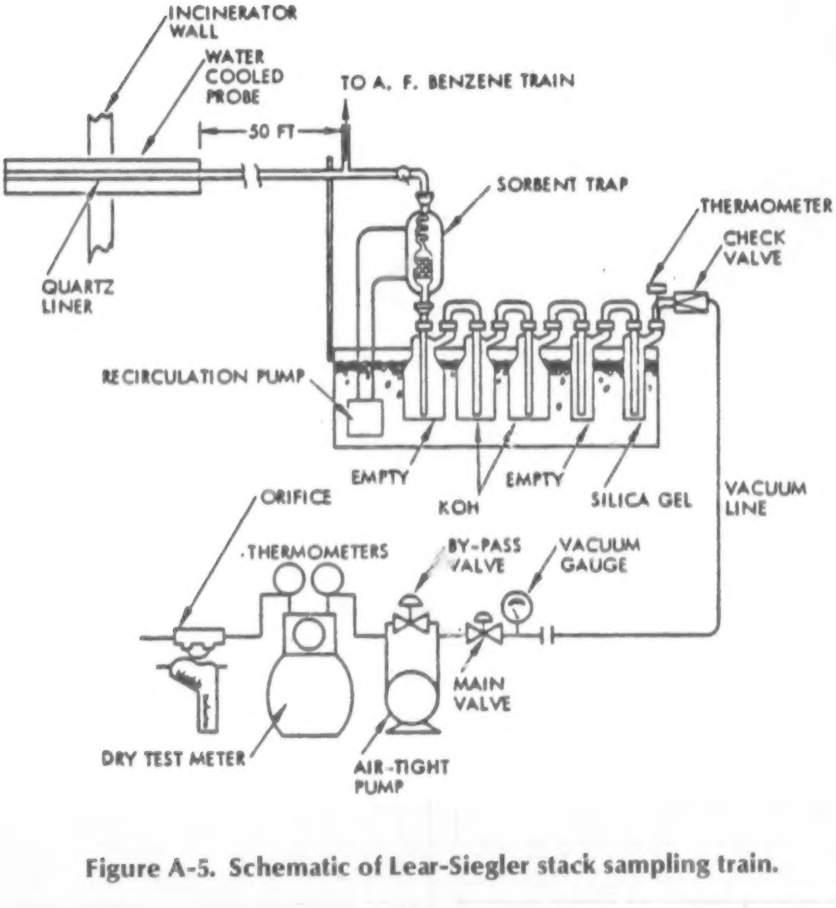
INCINERATOR WALL
WATER COOLED PROBE
TO A. F. BENZENE TRAIN
50 FT
SORBENT TRAP
THERMOMETER
CHECK VALVE
QUARTZ LINER
RECIRCULATION PUMP
EMPTY
KOH
EMPTY
SILICA GEL
VACUUM LINE
ORIFICE
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

Figure A-5. Schematic of Lear-Siegler stack sampling train.

hexane extracts with concentrated sulfuric acid until the acid fraction becomes only slightly colored. The acid wash is followed by a 10 mL water wash, followed by evaporation to dryness at room temperature using a stream of dry air. The sample is then redissolved in hexane and further purified by silica gel column chromatography as well as alumina column chromatography. The final eluate of the alumina column is concentrated to 200 μL prior to analysis.

Neutral Extraction Method

A typical neutral extraction technique for TCDDs consists of extracting with hexane (19). The hexane solution is chromatographed using a magnesia-celite 545 column, an alumina column, an alumina minicolumn, and finally a florisil minicolumn. The florisil column is eluted with methylene chloride which is concentrated to a volume of 60 μL in preparation for analysis (22).

Even with such elaborate separation techniques the 2,3,7,8-TCDD isomer is not resolved from other TCDD isomers. As a result, quantitative data must be considered a maximum level rather than an absolute level. Dow Chemical Company has devoted much effort to separation of the 22 TCDD isomers and presently can separate the 2,3,7,8-isomer from the 21 isomers. The Dow method (23) uses benzene Soxhlet extraction of a silica gel bed containing the collected chlorinated dioxins. The benzene extract is passed through a series of four column chromatography steps. These columns are: (1) silica over acid modified silica, (2) sodium hydroxide modified silica over silica, (3) silver nitrate modified silica, and (4) basic alumina. The various chlorinated dioxin fractions are further separated by high pressure liquid chromatography and finally gas chromatography. Packed column gas chromatography results in the separation of a fraction containing the 2,3,7,8-isomer plus a maximum of 11 additional isomers, whereas capillary gas chromatography separates the 2,3,7,8-isomer containing only two additional isomers.

Analytical methods for TCDDs must be able to differentiate between 2,3,7,8-TCDD and other similar compounds. The most common methods currently used for the detection of 2,3,7,8-TCDD are gas chromatography (10,13,14,17,24-28) and combined GC with mass spectrometry (18,19,21,29). Several authors have reported the analysis of 2,3,7,8-TCDD by the combination of gas chromatography and mass spectrometry (11,12,15,18,30-33). Due to availability and relative ease of application, gas chromatography was the first successful method applied. Early attempts were made using microcoulometric detection; however, the detection limit was inadequate. Currently, electron capture detection using ^{63}Ni is being used and is achieving a detection limit of approximately 200 parts-per-trillion (27). Although tritium electron capture can be used, the detection limit is a factor of 5 to 25 times higher (13,24).

Mass spectrometry is the only known method that is capable of achieving a sensitivity of better than one part-per-trillion and also displaying a high degree of selectivity, when coupled with gas chromatography. By monitoring ions which are characteristic of 2,3,7,8-TCDD, m/e 320 and m/e 322, and using gas chromatographic retention times as well as the ratio of the intensities of m/e 320 to m/e 322, a highly sensitive method which is also highly selective is obtained. Unfortunately, as mentioned earlier, other compounds can contribute to the intensity at these two masses (34,35). Two approaches can minimize this problem.

The first approach utilizes high resolution mass spectrometry ($M/\Delta M > 9000$) to increase the selectivity. The ions at nominal mass 322 produced from 2,3,7,8-TCDD have $C_{12}H_4Cl_4O_2$ as their elemental composition and thus have an "exact" mass of 321.8936 due to the sum of the various mass defects. The ion current at nominal mass 322 from heptachlorinated biphenyl is due to ions of composition $C_{12}H_3Cl_5$ which have an "exact" mass of 321.8677. Therefore, by focusing on 321.8936 amu, only ions of the composition resulting from 2,3,7,8-TCDD are detected. It is possible to produce ions of composition $C_{12}H_4Cl_4O_2$ from other sources but by considering gas chromatographic retention times these interferences can usually be resolved. Although detection limits in the low parts-per-trillion region are attained without signal averaging, dramatic improvements in the signal-to-noise ratio can be observed when signal averaging is used (29,31,36,37).

A second approach uses low resolution mass spectrometry but includes a more selective separation step prior to the mass spectrometric analysis. Capillary column gas chromatography is usually used (30); however, liquid chromatography followed by capillary column gas chromatography has been shown to be even more successful (23). Both the high resolution and the low resolution mass spectrometric methods use internal standards for quantification. Most investigators are using ^{37}Cl-labelled 2,3,7,8-TCDD; however, recently ^{13}C-labelled 2,3,7,8-TCDD has been used (23).

An ideal gas chromatographic/mass spectrometric analysis technique for 2,3,7,8-TCDD is the combination of high resolution capillary column gas chromatography and high resolution mass spectrometry. This combination provides the required sensitivity as well as the selectivity needed to differentiate 2,3,7,8-TCDD from the many interferences present in environmental samples.

Recent analytical methodologies using negative ion chemical ionization mass spectrometry have been published. An early communication by Hunt and coworkers (38) reported a signal-to-noise ratio of 50 from a 2 pg direct probe insertion sample using oxygen as the reagent gas. A sensitivity 25 times higher than the direct probe insertion method using electron impact ionization is reported. A recent paper by Hass, *et al.* compares the relative sensitivities of various chemical ionization modes. Positive ion versus negative ion chemical ionization modes using methane, oxygen, and mixed methane/oxygen reagent gases are compared (39). Positive ion chemical ionization is found to afford the greatest sensitivity; however, ions indicative of the molecular weight are not produced.

After all factors of extraction and sample cleanup have been performed and analytical methods evaluated a series of criteria must be met for the confirmation of 2,3,7,8-TCDD. These have been described by Harless, *et al.* (37) as shown in Table A-8.

DISCUSSION/RECOMMENDATIONS

The preparation of environmental samples for TCDD analyses involves two major steps, the extraction of the sample and cleanup of the sample. Extraction with a strong base designed to remove phenolics from nonphenolics is the most widely used sample extraction for TCDDs. Experiments with samples spiked with higher PCDDs have shown no evidence of TCDD formation resulting from extraction with alkali. Neutral pH extraction procedures for TCDDs in tissues have been investigated. These seem to be somewhat more complicated than the strong base extraction procedure. However, neither of the preceding two methods of sample preparation are infallible. Environmental contaminants such as DDE, DDT, and PCBs will be extracted with TCDDs and interfere in the GC/MS final step. Column chromatography is

TABLE A-8. CRITERIA UTILIZED FOR CONFIRMATION OF 2,3,7,8-TCDD RESIDUES

(1) Correct capillary column GC/HRMS retention time of 2,3,7,8-TCDD.

(2) Correct chlorine isotope ratio of the molecular ion (m/e 320 and m/e 322).

(3) Correct capillary column GC/HRMS multiple ion monitoring response for TCDD masses and $^{37}Cl_4$-TCDD mass (simultaneous response for elemental composition of m/e 320, m/e 322, and m/e 328).

(4) Correct response for coinjection of sample fortified with $^{37}Cl_4$-TCDD and 2,3,7,8-TCDD standard.

(5) Response of m/e 320 and m/e 322 must be greater than 2.5 times the noise level.

Supplemental criteria which may be applied to samples from highly contaminated sources

- (A) COCl loss indicative of a TCDD structure
- (B) Capillary column GC/HRMS peakmatching analysis of m/e 320 and m/e 322 in real time to confirm the TCDD elemental compositions.

preferable using two basic alumina columns with hexane, carbon tetrachloride, and methylene chloride as eluants. The method of choice for the analysis of TCDDs is combined GC/MS. This technique has the sensitivity and specificity to give TCDD analyses in the ppt range provided there has been suitable sample preparation and cleanup beforehand.

Capillary column GC is being extensively used for TCDD determinations for several reasons. Capillary GC columns reduce the number of components found in any single resolved GC peak reducing the possibility of interferences from co-elution of other compounds. Also, the higher resolution of capillary GC columns permits separation of closely related isomers and the sharp peaks produced increase the signal-to-noise ratio for each component. A disadvantage of capillary GC columns is sensitivity to the amount of sample injected and the column may then be destroyed if too much material is present in the sample.

Packed columns are recommended for screening of samples for PCDDs where high resolution of capillary columns is not needed. The MS portion of the GC/MS system provides the specificity needed for low-level analyses. Two types of mass spectrometers are available for TCDD analysis: low resolution instruments (LRMS) and high resolution instruments (HRMS). A LRMS measures ions to the nearest whole mass unit. A HRMS instrument on the other hand is able to measure ions of exact mass, i.e., HRMS can differentiate between two ions whose exact mass may differ by only 0.002 mass unit or less. LRMS is less expensive than HRMS, both in initial instrument purchase and routine maintenance costs. As a screening technique, LRMS is well suited, although it permits some false positives to be tagged for further work. For a determination of TCDD and other tetrachloro-isomers in a sample, either LRMS or HRMS may be used. However, for a specific 2,3,7,8-TCDD determination, capillary column GC with HRMS is a necessity to separate 2,3,7,8-TCDD from other isomers and to ensure that the sample does not show any interferents.

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SAMPLING AND ANALYSIS PROCEDURES FOR FORMALDEHYDE

BACKGROUND

Formaldehyde is a colorless gas with the chemical and physical properties outlined in Table A-9.

TABLE A-9. CHEMICAL AND PHYSICAL PROPERTIES OF FORMALDEHYDE

Property	Value
Formula	HCHO
Molecular weight	30.03
Physical state	Gas
Melting point	−92°C
Boiling point	−21°C
Density	0.815 (20°C)
Refractive Index	1.075 (air = 1.0)
Solubility	Soluble in water, alcohol, acetone, and benzene

Formaldehyde is readily soluble in water and is marketed chiefly as an aqueous solution, although solutions in methanol, propanol, and butanol are commercially available. Formaldehyde is produced principally from the catalytic oxidation of methanol, although appreciable quantities are also derived from the direct oxidation of hydrocarbon gases.

Formaldehyde has a pungent odor and formaldehyde solutions and vapors are highly irritating to the mucous membranes of the eyes, nose, and upper respiratory tract. The threshold value for these effects is as low as 5 ppm (V/V) in air (1).

SAMPLING AND ANALYSIS

Meier (2) has examined various plastic bags for collecting various pollutant gases, including formaldehyde, and found FEP bags (25067-11-2) preferable to Mylar, aluminum foil, and scotchpak. Activated 13X molecular sieve was found to be an excellent solid sorbent for sampling acrolein and low molecular weight aldehydes and ketones in air [Gold, *et al.* (3)]. Yokorchi, *et al.* (4) also used sorbent tubes of 13X molecular sieve for formaldehyde sampling of ambient air. The tubes were thermally desorbed and analyzed by GC/MS.

Ootsuka, *et al.* (5,6) used triethylamine treated filter paper for trapping formaldehyde, nitrogen dioxide, and sulfur dioxide. The formaldehyde was extracted with water and determined spectrophotometrically using the 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole method. This same reagent was used for the determination of formaldehyde in air by an anonymous author (7). Samples were collected using a water scrubber.

Spincer and Chard (8) determined formaldehyde in cigarette smoke using the p-rosaniline-SO_2 spectrophotometric method. A new spectrophotometric method for the determination of formaldehyde in air was reported by Nair and Guptu (9). The method is based on the reaction of formaldehyde with Cu(II) and oxalydihydrazide.

Several researchers have used the chromotropic acid method for the analysis of formaldehyde in ambient air samples, although the sampling methods varied. Smith (10) collected formaldehyde from industrial emissions in a 1 percent sodium bisulfite ($NaHSO_3$) solution in Greenberg-Smith impingers. The sampling rate was 0.5-1.0 ft^3/min. Several tentative methods of the American Industrial Health Association (AIHA) use this same method (11), and it is the standard NIOSH procedure for formaldehyde in air (12). The chromotropic acid methods tend to be sensitive to interferences and lack the stability and selectivity for combustion applications.

Klochkouskii, *et al.* (13,14) used 1:200 HCl bubblers and H_2O bubblers for sampling exhaust gases of internal combustion engines. NO_x interference in the chromotropic acid procedure was eliminated by the addition of sulfanilic acid. Five-liter samples were taken at a rate of 20 L/hr.

Andynkova, *et al.* (15) used evacuated bottles for collecting air samples polluted with engine exhaust. The samples were analyzed using an improved chromotropic acid method, in which the sulfuric acid concentrations were increased to 60-70 percent.

Olansky and Deming (16) optimized the absorbance response of formaldehyde in the chromotropic acid method with respect to the volumes of sulfuric acid and aqueous chromotropic acid.

Stahl (17) has reviewed methods for the determination of formaldehyde in atmospheric samples. Methods included chromotropic acid, J-acid, and phenyl-J-acid, and the Modified Schiff method using para-rosaniline in sodium tetrachloromercurate (II) and sodium bisulfite.

Several methods for atmospheric formaldehyde determination were compared by Izunikawa, *et al.* (18). These researchers found the p-rosaniline and 3-methyl-2-benzothiazolone methods to be equivalent in sensitivity and approximately 3.5 times more sensitive than chromotropic acid or the 4-amino-3-hydrazono-5-mercapto-1,2,4-triazole method.

The EPA/IERL Procedure for Level 2 sampling and analysis of organic materials uses the 3-methyl-2-benzo-triazolone hydrazone (MBTH) method for total aldehyde in air (19), as does the American Industrial Health Association (11). The aldehydes are collected in bubblers in a 0.05 percent aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) solution. The resulting azine is then oxidized by a ferric chloride-sulfamic acid solution to form a blue cationic dye in acid media for spectrophotometric determination.

Numerous papers have appeared in which 2,4-dinitrophenylhydrazine (DNPH) is used to trap and derivatize formaldehyde in gaseous samples. Smythe and Karasek (20) condensed engine exhaust gases at 0°C and reacted the aqueous distillate with DNPH for analysis by gas chromatography. Automobile exhaust gases were collected by condensation in liquid oxygen traps before reaction with a 0.1 percent solution of DNPH in HCl by Hoshika and Takatu (21). Analysis was by capillary column gas chromatography in an SF-96 column. Thirty-liter samples of exhaust were taken.

Formaldehyde and other oxygenated organic compounds were trapped using DNPH or small Tenax adsorption columns by Hagemann, *et al.* (22). The derivatives were analyzed by GC/MS. Kenmochi and Ishii (23) collected atmospheric aldehyde in DNPH solution for analysis by gas chromatography. Mansfield, *et al.* (24) analyzed formaldehyde in tobacco smoke by reaction with DNPH followed by separation and quantification by HPLC on 10 μ silica columns.

Aliphatic and aromatic aldehydes in urban air, industrial emission, auto exhaust, and tobacco smoke were collected in bubblers containing DNPH solution by Kuwata, *et al.* (25). Five- to 30-liter samples were taken at 0.5 to 1.5 L/min for analysis by reversed phase HPLC and an RP-18 column.

Grosjean, Furg, and Atkinson (26) used impingers with DNPH solution and DNPH impregnated glass bead cartridges for sampling air for formaldehyde and other aldehydes with analysis by HPLC with UV detection. Six-liter samples were collected at a rate of 1 L/min with collection efficiencies for formaldehyde of 90 percent for impingers and 26 to 86 percent for the cartridges, depending upon the humidity.

Formaldehyde and other aldehydes and ketones were measured by Smith, *et al.* (27) in vehicle exhaust by collecting samples at 4 L/min in midget impingers containing DNPH in dilute HCl. Analysis was by gas chromatography with a column of 6.7 percent Dexsil 300 GC on DMCS/AW Chromosorb G. Hall (28) used impingers of DNPH in acetonitrile for collecting aldehydes in air with analysis by HPLC with UV detection. Air was sampled at a rate of 6.5 L/min for 60 minutes. Beasley, *et al.* (29) trapped formaldehyde from air with adsorption tubes of silica gel impregnated with DNPH. The tubes were desorbed with CH_3CN and analyzed by reversed phase HPLC on a C_8 column.

Formaldehyde was collected on sorbent tubes of impregnated charcoal, which converted it to formic acid by Kim, *et al.* (30,31). After desorption with dilute H_2O_2, the formic acid was determined by ion chromatography. Twenty-liter air samples were taken at 100-200 mL/min.

Day, *et al.* (32) used chemical ionization mass spectrometry for the simultaneous determination of low molecular weight aldehydes in automobile exhaust.

Formaldehyde in air was determined using gas chromatography secondary ion mass spectrometry (GC/SIMS) by Hokohu (33). Samples were concentrated on Carbosieve B.

Vehara, *et al.* (34,35) used a sensitive microwave cavity spectrometer for direct detection of formaldehyde in automobile exhaust. Concentrations as low as 0.2 ppm could be measured directly using the $7_{25} - 7_{26}$ rotational line.

A versatile IR gas analyzer employing gas filter correlation techniques was used to measure gaseous pollutants in automobile exhaust by Burch, *et al.* (36). The minimum detectable concentration of formaldehyde is 0.05 ppm.

Formaldehyde and furfural were determined in industrial air by Zaitseva, *et al.* (37) using a.c. polarography. Polarography was also used by Kven and Ivanov (38) for formaldehyde

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determination in air at the 0.5 g/mL level. Other saturated and unsaturated aldehydes and ketones were found not to interfere.

A number of analytical techniques are available for the sampling and analysis of stack emission. The "older" methods tend to be less specific in that no chemical separation is involved in the analysis process. The most used procedure for sampling air and gaseous emissions for formaldehyde is the well known chromotropic acid procedure (11). In this method, formaldehyde is trapped from the gas phase by sampling with impingers or bubblers containing 1 to 10 percent aqueous sodium bisulfite ($NaHSO_3$). An aliquot of this solution is then reacted with chromotropic acid-sulfuric acid solution to form a purple monocationic chromogen. The absorbance is read at 580 nm, and is proportional to the quantity of formaldehyde in solution. The proposed reactive scheme for this method is shown in Figure A-6.

The chromotropic acid method suffers from a number of shortcomings. Although aldehydes and ketones do not interfere significantly, aromatic hydrocarbons and olefins can cause serious interference. Also, compounds that are easily converted via hydrolysis or oxidation to formaldehyde in strong, warm sulfuric acid may also interfere. Phenols cause a negative interference when present at an eight fold excess over formaldehyde. A slight interference occurs from dienes. Although ordinary quantitites of sulfur dioxide and nitrogen dioxide do not interfere, the high concentrations of these species in exhaust gases may be another matter, although several papers reported masking the effects of nitrogen dioxide by the addition of sulfanilic acid.

The remaining colorimetric methods also do not appear to be suitable for accurate estimation of formaldehyde emissions from stacks. The MBTH method is not specific for formaldehyde in that other water soluble aliphatic aldehydes interfere (e.g., acetaldehyde).

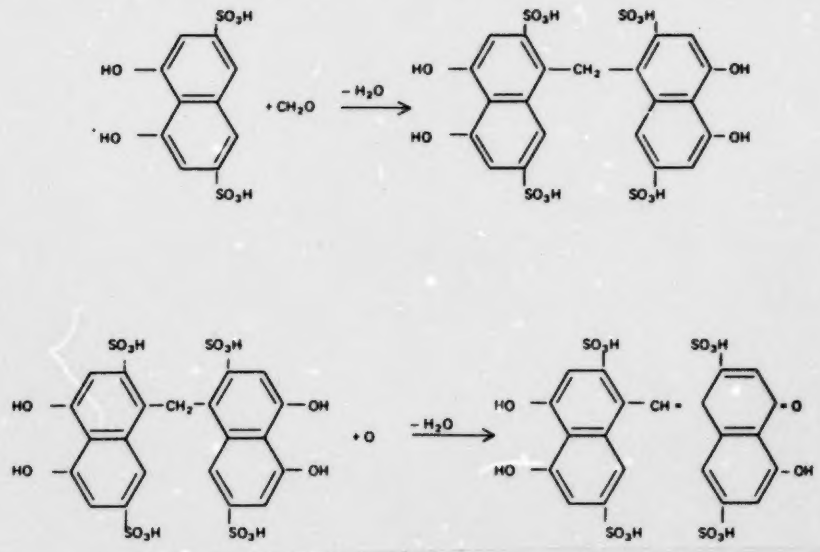

Figure A-6. Reaction of formaldehyde with chromotropic acid.

DISCUSSION/RECOMMENDATIONS

The sampling method which appears to have received the most attention in recent investigations is the DNPH trapping method with analysis of the resulting hydrazone derivative by liquid or gas chromatography (21,24). This method offers several advantages over the colorimetric procedures. The most obvious advantage is that formaldehyde is trapped as a stable species at the time it is sampled. In this procedure, formaldehyde containing effluent is trapped in impingers or bubblers containing 2,4-dinitrophenylhydrazine in dilute (1N) hydrochloric acid. The formaldehyde reacts to form the 2,4-dinitrophenylhydrazone as shown in Figure A-7. This derivative, along with the hydrazone derivatives of other aldehydes and ketones in the effluent are extracted in pentane or other water immiscible organic solvent, concentrated, and exchanged to an appropriate solvent and volume for chromatographic analysis. Separations have been achieved by both HPLC and GC. The advantage of a chromatographic method is the increased specificity and sensitivity over colorimetric procedures.

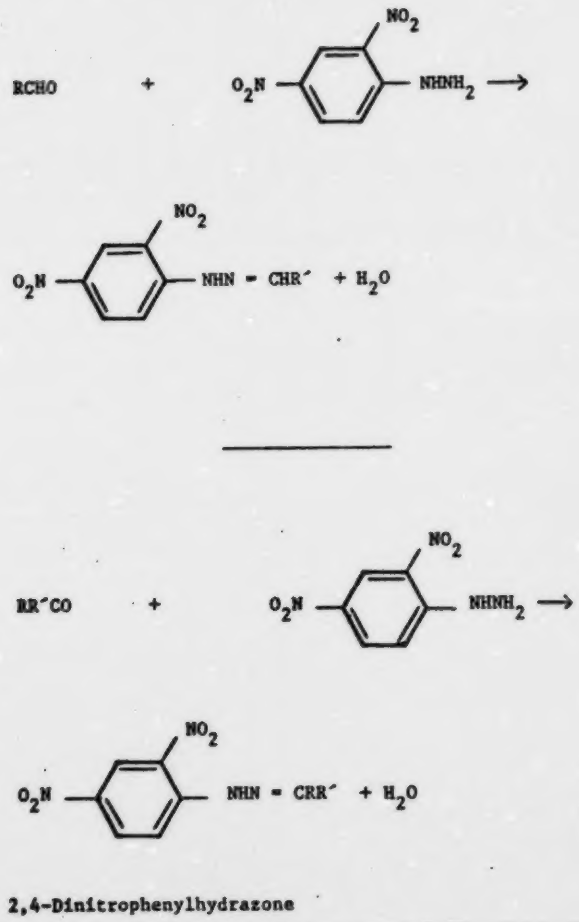

Figure A-7. Reaction of 2,4-dinitrophenylhydrazine with aldehydes and ketones.

The choice of chromatographic methods depends upon the complexity of the resulting DNPH extract. With gas chromatography as the separation method, the variety of detectors available should allow very sensitive determination of the derivative. Coupling the GC to a mass spectrometer would enable precise identification of the formaldehyde. Using liquid chromatography, the detector of choice would be a variable wavelength UV with detection at 340 to 360 nanometers, the γ_{max} of this class of compounds. Operation at these wavelengths will give added specificity to the analysis. The HPLC/MS interface is another possibility, although detection limits for this method are not well established (39). A summary of the various sampling and analysis methods for formaldehyde is shown in Table A-10.

TABLE A-10. STACK SAMPLING AND ANALYSIS METHODS FOR FORMALDEHYDE

Method	Advantages	Disadvantages
Colorimetric methods		
Chromotropic acid-(bisulfite trapping)	NIOSH and AIHA standard method; inexpensive; specific for formaldehyde	Many interferences in stack emissions
MBTH	Standard method	Not specific for formaldehyde
Instrumental methods		
DNPH-HPLC or DNPH-GC	Stable derivative formed upon sampling; low detection limit; chemical separation	More expensive for analysis than colorimetric methods
Tenax-GC or Tenax-GC-MS	Very specific (MS)	Low sampling volumes; very expensive (MS)
Molecular or chromatographic solvent and GC or GC-MS	Very specific (MS)	Very expensive (MS); not much work done on recoveries for these solvents

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SAMPLING AND ANALYSIS PROCEDURES FOR POLYNUCLEAR AROMATIC HYDROCARBONS INCLUDING BENZO[A]PYRENE

BACKGROUND

Polynuclear aromatic hydrocarbons (PAH) are a unique class of organic compounds composed of a series of fused rings. These compounds are characterized by alternating double bonds capable of sustaining a delocalized electronic ring current. This property is called aromatic resonance, a term used to indicate that the molecule will have conjugated (π) electrons in each five-, six-, or seven-membered ring (usually six); the condensed ring structure will be flat and the resultant aromatic molecule will have far greater chemical stability than similar olefinic hydrocarbons without resonance. Benzene, the parent of most PAH, has an excess 36 kcal/mole as defined by heat of hydrogenation compared to unsaturated cyclohexane without resonance. It is important to note that many acronyms are used to abbreviate this family of compounds: POM, PNA, PNAH, PNH, PCH. However, PAH will be used in this report to mean the biologically important aromatic hydrocarbons, principally benzo[a]pyrene, including compounds such as benzo[a]anthracene, 3-methylcholanthrene, dibenzo[a,h]anthracene and 7,12-dimethylbenzo[a]anthracene, all cited in the literature as highly carcinogenic or mutagenic. The importance of limiting the scope of PAH measurements to a finite list of compounds is highlighted by the work of Snook and co-workers who identified over 900 PAH species from cigarette smoke condensate (1). Several hundred PAH and derivative compounds have been identified from fossil fuel combustion products (2-7) and most have no reported mutagenic or carcinogenic characteristics.

The production of PAH in the residential and commercial combustion of fossil fuels was reported in the classical study of Hangebruack, von Dehnden, and Meeker at the U.S. Public Health Service (8). They measured the production of benzo[a]pyrene (BaP) relative to gross heat input for several furnace types. As shown in Figure A-8, efficient, high-heat furnaces are seen to greatly reduce BaP emissions over inefficient, residential combustion units. The effect of reduced heat flux on BaP emissions is seen for the case of coal combustion, where starved air and incomplete combustion lead to the production of fused ring aromatics.

Table A-11 shows a comparison of both BaP and total BaP emissions per year in the United States as a function of source type (9,10). Total PAH emissions are difficult to compile since the available data represent different analytical methods, measurement of different PAH species, and the reported data are usually taken at different times. However, these tabulations do point to wood combustion as the single largest contributor to ambient PAH levels. This is interesting since wood fuel, unlike coal, does not contain fused-ring aromatics in the raw fuel. These data indicate that most stationary source PAH arise from pyrosynthesis during the combustion of wood. The BaP emissions reported in Table A-11 represent a concerted study performed in the 1960s to evaluate PAH emissions using BaP as an indicator. In this early study, coal was seen to be the preponderant source of BaP emissions in the U.S., a fact that reflects the shift away from coal as a residential fuel in the last two decades. These data also are indicative of a great improvement in ambient air quality in the past decade.

The principal PAH emissions measured in coal-fired power plants are hydrocarbon species although some nitrogen and sulfur containing PAH have been reported at very low levels with respect to their hydrocarbon analogs (10). Important heteroatom species reported in this

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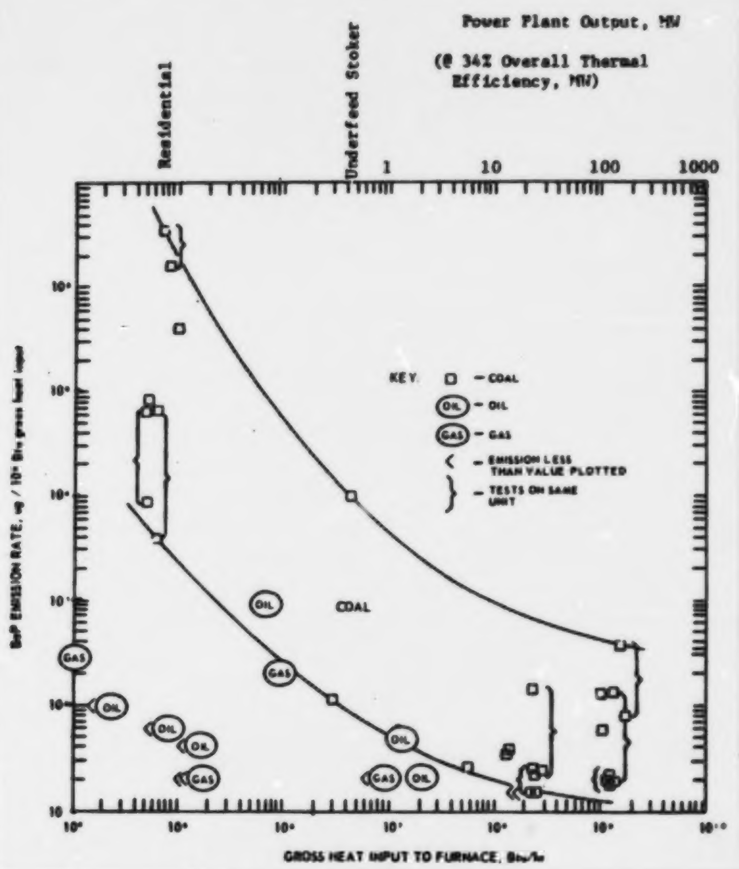

Figure A-8. Range of benzo[a]pyrene emissions from coal, oil, and natural gas heat-generation processes.

literature include dibenzo[c,g]carbazole, 2-ethyl-5-isoamylthiophene, t-butyl phenol, and ethylbenzaldehyde. In a recent study, Zelenski and co-workers have summarized the reported PAH species emitted from fossil fuel combustion for power generation (11).

Since a single group of species, representative of carcinogenic PAH emissions, has not been classified, it is instructive to examine the structure-activity relationships used to identify compounds believed to pose the greatest potential as carcinogens. The model for structure-activity of PAH, currently having the greatest scientific acceptance, is the "bay-region" theory of Jerina, *et al.* (12,13). PAH species that show high mammalian carcinogenicity are often found to contain a phenanthrene structure such that the U-shaped angle of this fused, three-ring structure forms an indentation or bay (13). The predominant chemical pathway to activation of bay-region PAH involves oxidation. Often an epoxy-diol structure is the active biometabolite. Typical bay-region structures and their oxidized forms are shown in Figure A-9. The pathway to biological activation of BaP is shown in Figure A-10. Here cytochrome P-450 oxidizes the arene ring first to the oxide which is then hydrated to the dihydrodiol; then further oxidation occurs to a diol epoxide. This pathway is believed to generate an important ultimate carcinogenic form of benzo[a]pyrene, B[a]P-7,8-diol-9,10 epoxide (14,15).

TABLE A-11. ESTIMATE OF BaP AND PAH SOURCE EMISSIONS IN THE UNITED STATES

Source	BaP Emissions—1960s(9)		Total PAH Emissions—1970s(10)	
	Metric tons/year	Percent	Metric tons/year	Percent
Open Burning	502	43	4,025	37
Coal refuse	308	27	29	<1
Forest and agricultural	127	11	3,910	36
Vehicle disposal	45	4	—	—
Miscellaneous	22	2	86	<1
Coal Combustion	391	33	184	2
Residential hand-stoked	381	33	102	1
Chain-grate and spreader stokes	9	<1	69	<1
Coal-fired power plants	1	<0.1	13	<0.2
Coke Production	181	16	632	6
Wood Combustion	36	3	3,839	35
Enclosed Incineration	22	2	56	0.5
Vehicular Emissions	20	2	2,266	21
Petroleum Production	5	0.5	4	<0.1
Oil Combustion	2	<0.2	7	<0.1
Total	1,159		10,013	

Recently a considerable interest has focused on heteroatom substituted PAH species such as nitro-PAH (16-18) identified as high-activity carcinogens found in diesel exhaust. These species may be reaction products between PAH and NO_2 in coal-burning power plants (19,20). In a related study, researchers at the Oak Ridge National Laboratory are actively investigating the presence of basic, nitrogen containing PAH species, such as primary aromatic amines and multiring azaarenes that show higher mutagenic activity than their hydrocarbon parents and are found in fossil fuels (21).

At the present time, the mutagenic and carcinogenic properties of heteroatom PAH are incompletely understood. Nitro and oxygenated PAH have been found to be mutagenic with activation (22) and a nonmutagenic PAH became an active bacterial mutagen after reaction with NO_2 (23). Sulfonated PAH species have also been reported to be mutagens (24); thus, due to stack SO_3 they must also be suspect carcinogens. A representative list of suspect

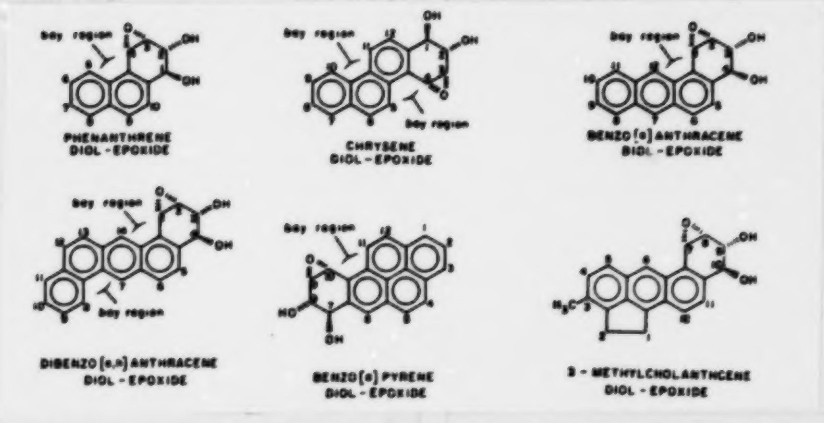
bay region
PHENANTHRENE DIOL-EPOXIDE
CHRYSENE DIOL-EPOXIDE
BENZO[a]ANTHRACENE DIOL-EPOXIDE
DIBENZO[a,h]ANTHRACENE DIOL-EPOXIDE
BENZO[a]PYRENE DIOL-EPOXIDE
3-METHYLCHOLANTHCENE DIOL-EPOXIDE

Figure A-9. Benzo-ring diol epoxides showing the "bay-region" structures.

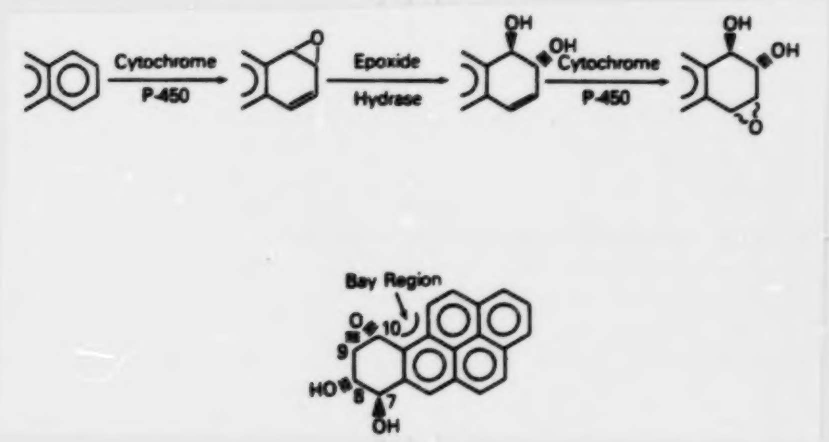
Cytochrome
P-450
Epoxide
Hydrase
Cytochrome
P-450
OH
Bay Region
HO
7
8
9
10

Figure A-10. Oxidative activation of PAH to the diol epoxide form.

carcinogenic PAH for their precursors should be established so that a validated screening procedure can be applied to stack emission measurements.

SAMPLING METHODS

Air sampling techniques have been discussed earlier in this report, and the methods most often used for PAH analysis include filtration of particulate matter at elevated temperatures followed by condensation of the PAH containing organic fraction. Figure A-11 shows a diagram of a typical resin bed collector that is placed after the heated filter in a modification of the Method 5 sampling technique. The physical arrangement of a sorbent collector in the Modified Method 5 train is shown in Figure A-12 (25). This collector has been described in several articles by Jones and co-workers (26-29) and has been used to collect and measure representative PAH in emissions from coal-fired residential and commercial boilers (30-32). This system normally operates at 0.75-1 scfm to collect 5-7 m^3 of stack gas in a representative

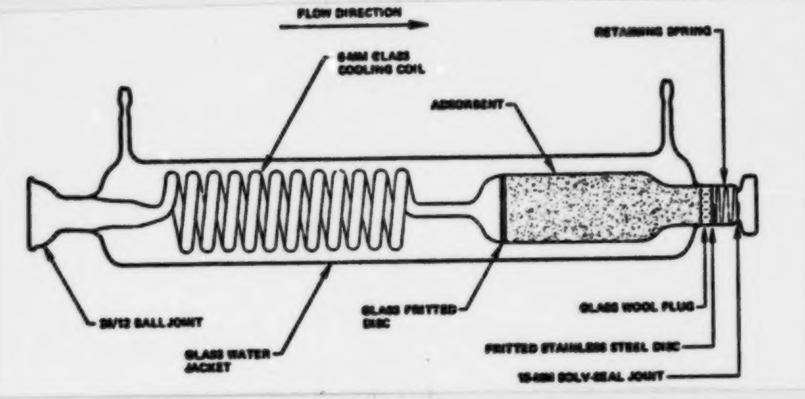
FLOW DIRECTION
RETAINING SPRING
6-MM GLASS COOLING COIL
ADSORBENT
28/12 BALL JOINT
GLASS WATER JACKET
GLASS FRITTED DISC
GLASS WOOL PLUG
FRITTED STAINLESS STEEL DISC
10-MM SOLV-SEAL JOINT

Figure A-11. Typical resin bed collector.

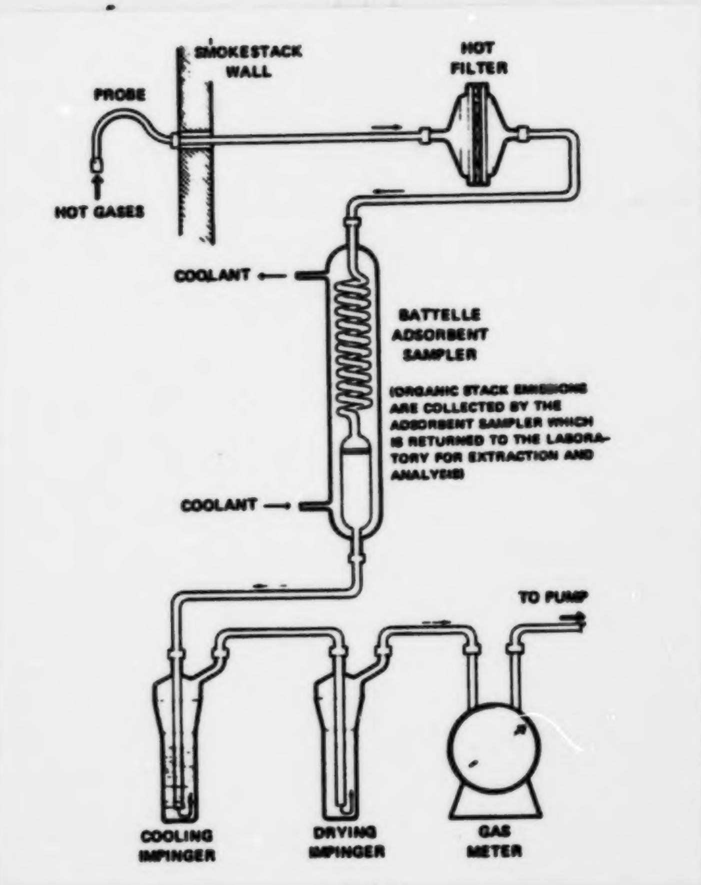
SMOKESTACK WALL
HOT FILTER
PROBE
HOT GASES
COOLANT
BATTELLE ADSORBENT SAMPLER
(ORGANIC STACK EMISSIONS ARE COLLECTED BY THE ADSORBENT SAMPLER WHICH IS RETURNED TO THE LABORATORY FOR EXTRACTION AND ANALYSIS)
COOLANT
TO PUMP
COOLING IMPINGER
DRYING IMPINGER
GAS METER

Figure A-12. Schematic of combustion effluent sampling system.

sample. A similar sorbent collector can be used with the SASS train to collect a much larger gas sample, 30 m^3 (33-34). Figure A-13 shows a schematic of a high capacity sorbent collector that can be used to collect these larger stack samples.

Although Tenax and XAD-2 resin materials have both been used to adsorb volatile PAH species, XAD-2 is generally preferred for semivolatile PAH. Tenax is preferred for volatile species such as benzene when heat desorption is the mode of recovery although Tenax is expensive and degrades to several diphenyl quinones if exposed to the hot, oxidizing climate of stack gas emissions (29). Both XAD-2 and Tenax have been shown to have a high collection efficiency for PAH (35-36). Consistent with the EPA Level 1 analysis procedures methylene chloride is the solvent of choice in extracting PAH compounds from the XAD-2 resin bed.

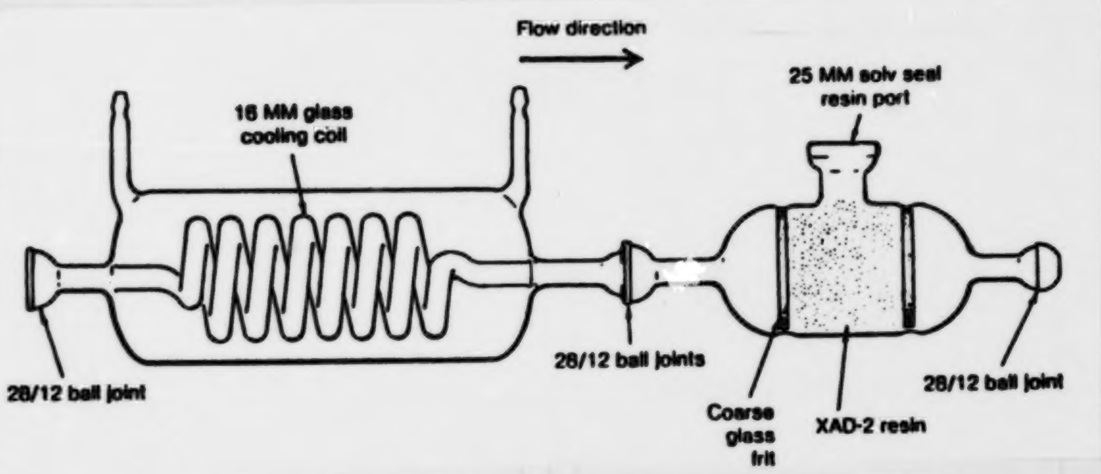

Figure A-13. High capacity adsorbent sampling system for PAH.

Although resin extraction is straightforward, recovery of PAH compounds from particulate samples can be very difficult. Depending on the nature of the active adsorption sites on the collected particulate, PAH recoveries can be highly solvent dependent (37-39). On very adsorptive particulate surfaces some authors suggest supplementing the methylene chloride/ Soxhlet extraction of fly ash with a 24-hour Soxhlet extraction with a higher boiling solvent such as o-dichlorobenzene or toluene (40) or subjecting the particulate and filter to ultrasound and ultrahigh speed mixing to efficiently extract PAH (41). Accurate characterization of PAH condensed onto fly ash is further complicated by the problems of artifact formation on the filter (42) and vaporization of PAH off the particle surface when exposed to the stream of hot sample gas (43). The problem of collection and recovery of particulate-associated PAH are treated in two monographs on PAH methods; one by White and Vanderslice (44) and another by Buttler (45).

ANALYTICAL PROCEDURES

The available analytical methodologies used to measure PAH in power plant emissions fall into two broad categories, screening and molecular analysis. Typical screening procedures include fluorescence (46), UV absorption (47), synchronous fluorescence (48-49), spot tests (50), thin-layer chromatography (TLC) (51-52), channel TLC (53), X-ray optical luminescence

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(54), and magnetic circular dichroism (55). The two screening procedures that have experienced the highest degree of validation are an instrumental TLC procedure for BaP and the naphthalene-enhanced fluorescence spot test for total PAH. The scanning TLC procedure (56) involves the separation of benzo[a]pyrene from other chemical species using an acetylated cellulose substrate and optical isolation of BaP by direct reflectance fluorescence from the TLC plate. Swanson and co-workers were able to accurately screen 30-40 samples per day for BaP using this technique (56).

Figure A-14 shows the normalized excitation and emission fluorescence spectra for a series of PAH (57). This figure illustrates the problems associated with using fluorescence (or UV absorption) directly for screening PAH. Choosing a single wavelength which is characteristic of all possible PAH species is difficult. Additional problems occur in measuring PAH in real samples. Shifts in wavelength maxima are observed in solution measurements as a function of solvent strength. Increased solvent polarity often generates a bathochromic shift in PAH, Π → Π transitions. A second problem with solution optical spectroscopy is the quenching effect whereby another species in solution suppresses the native PAH fluorescence of the species of interest by intermolecular deactivation. Sawicki, *et al.* have observed this phenomenon arising from nitrobenzene and nitromethane (58). In a complex combustion sample, the possibility of a non-PAH compound contributing an interference signal precludes the use of direct fluorescence or UV absorption as a viable screening technique unless a preseparation is performed on the sample extract.

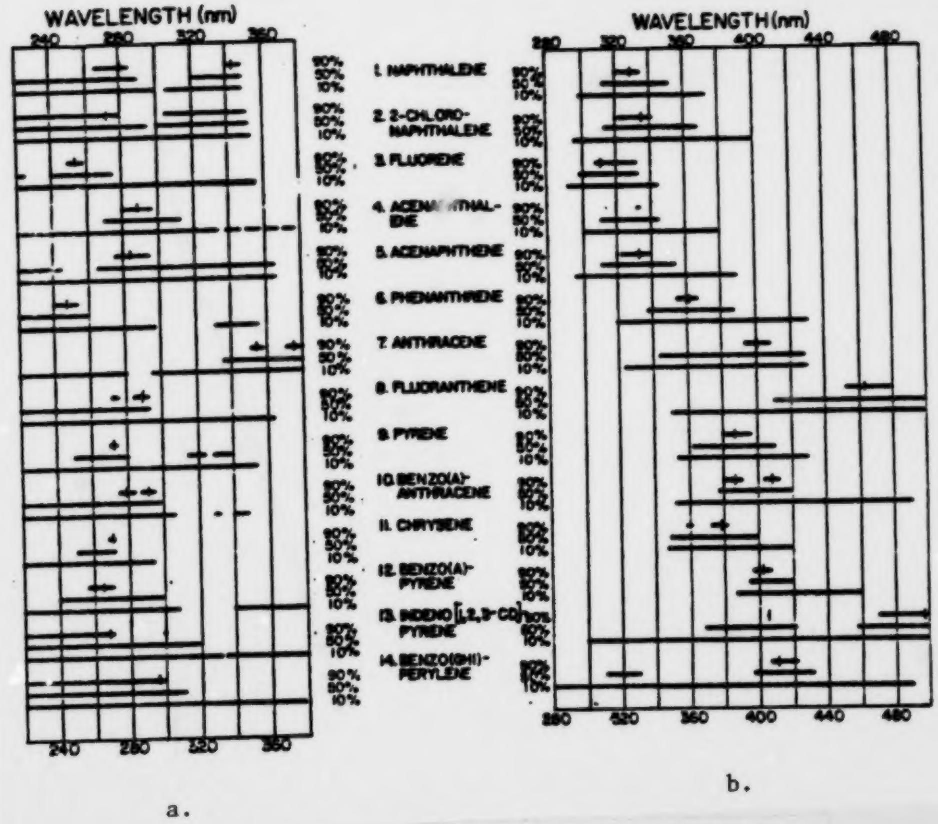

Figure A-14. Normalized fluorescence spectra of PAH.

An ingenious screening procedure based on naphthalene enhanced fluorescence has been extensively validated by EPA Industrial Environmental Research Laboratory at the Research Triangle Park, North Carolina (59). In this procedure, a portion of the sample extract is transferred to filter paper along with a highly concentrated naphthalene solution. After solvent vaporization the unknown molecular species are entrained in a crystalline naphthalene matrix. In the naphthalene matrix, the PAH analyte is pumped by vibrational coupling with the more energetic excited states of naphthalene to produce an amplified fluorescence. This enhanced or amplified fluorescence is easily detected visually. In optimum compounds, e.g., fluoranthene, a sensitivity of 7-10 picograms has been reported for this spot test. Although subject to potential interferences, this low-cost test is an excellent rapid screening procedure to identify samples to be carried forward for more expensive analyses.

Numerous analytical procedures have been proposed for PAH analysis. Of these, many are not suitable for the analysis of stack samples because of the complex matrix generated by this organic-rich source. Suitable candidate procedures involve three discrete steps—concentration, separation, and quantitative detection. Concentration is required due to the low levels of single molecular species found in stack emissions. If the PAH are collected via a Modified Method 5 or SASS train collector, the various sections of these collection devices must be rinsed and extracted with a suitable solvent, usually methylene chloride, noting, however, the problem of recovering BaP from particulate samples using this solvent. PAH containing solutions can be effectively concentrated by using a Kuderna-Danish concentrator, and final solvent blow-down can be achieved with clean, dry nitrogen. Higgins and Guerin (60) have identified a carryover problem with volatile PAH from such evaporative concentration techniques and suggest an ancillary Tenax collector to prevent loss of volatile PAH such as naphthalene during concentration.

Separation procedures for PAH often involve using gas chromatography (GC) because of the versatility of GC for volatile compounds such as 2-6 ring PAH species. PAH often have high melting and boiling points as shown in Table A-12 (61).

TABLE A-12. MELTING POINTS AND BOILING POINTS OF SOME TYPICAL PAH SPECIES

Compound	Number of rings	Melting point, °C	Boiling point, °C
Anthracene	3	216	340
Naphthalene	4	357	Sublimes
Picene	5	368	519
Coronene	6	438	525
Benzo[a]anthracene	4	158	Sublimes
Benzo[a]pyrene	5	176	—

Although the boiling points of many 3-6 ring PAH compounds are well above the operating temperature limit of about 300°C for most practical GC stationary phases, most PAH have a native volatility in the solid phase which allows them to vaporize at normal GC operating temperatures. This volatility is illustrated by the low enthalpies of sublimation measured by Murray, *et al.* (63) and the equilibrium vapor concentrations at 300°C which are calculated from the vapor pressure equations developed by Murray, *et al.* (64). These parameters are shown for several PAH compounds in Table A-13.

TABLE A-13. ENTHALPY OF SUBLIMATION AND EQUILIBRIUM VAPOR CONCENTRATION (EVC) OF SOME PAH COMPOUNDS

Compound	H° Sublimation (kJ/mole)	EVC at 300°C (g/m^3)
Pyrene	—	2.4×10^3
Benzo[a]anthracene	113 ± 2	2.4×10^3
Benzo[a]pyrene	118 ± 2	3.5×10^2
Benzo[k]fluoranthene	130	5.8×10^2
Benzo[ghi]perylene	128 ± 2	4.4×10^1

A principal advantage of gas chromatography and, more recently, high performance liquid chromatography (HPLC) is the ability to isolate single PAH compounds from the complex mixtures found in environmental and source samples. Gas chromatographic techniques usually employ either the resolving power of a selective stationary phase (solvent selection) or the high efficiency of capillary columns (column efficiency). Table A-14 gives some stationary phases which have been used for PAH separation.

TABLE A-14. EXAMPLES OF STATIONARY PHASE MATERIALS PROPOSED FOR PAH ANALYSES BY GAS CHROMATOGRAPHY

Stationary phase	Limitations	Reference(s)
Dexsil 300/Dexsil 400 (Carboranemethylsilicone)	Will not separate some isomers, e.g, BaP/BeP	65-67
OV-7 (Methylphenylsilicone)	Will not separate some isomers	68
BMBT (Liquid crystal)	Low temperature stability	69

Several authors have reported high-efficiency, glass capillary column analysis of complex PAH samples (70-72). Figure A-15 illustrates the high resolving power of capillary column separation. In the chromatogram, a complete separation is observed for most PAH in this standard mixture. The difficult-to-separate pairs—anthracene/phenanthrene, benzo[e]pyrene/benzo[a]pyrene, perylene/benzo[k]fluoranthene, and benzo[a]anthracene/chrysene—are all found to be well separated by this column.

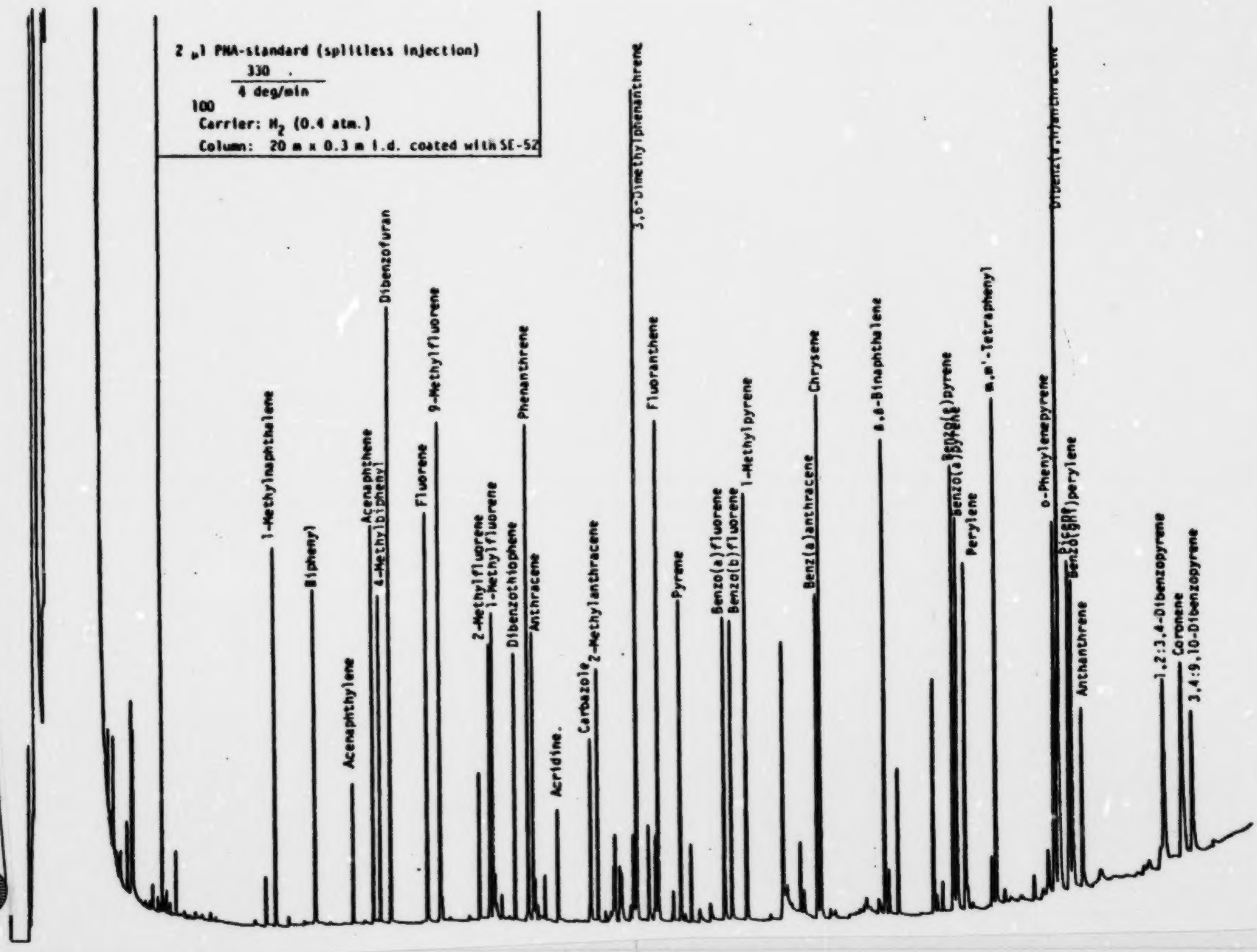

Figure A-15. GC chromatogram of polynuclear aromatic hydrocarbons separated on SE-52 capillary column.

Reproduced from best available copy.

In practice, even the high resolving power of capillary gas chromatography will not unequivocally identify an unknown molecular species as a PAH. A confirmatory technique, preferably one that can provide a quantifiable signal, is required to prove the identity of a suspect PAH. The technique which has received widest acceptance for this application is coupled GC and mass spectrometry (GC/MS). The current literature on PAH analyses is filled with references to the use of GC/MS, especially the combination of high-resolution capillary chromatography (HRGC) and mass spectrometry (73-78).

In a development document prepared for EPA Industrial Environmental Research Laboratory (RTP), Levins and co-workers developed five procedures suitable for the analysis of PAH sampled from coal- or oil-fired power plants using a SASS train or Modified Method 5 procedure (79). Two of these methods are screening procedures that use solution fluorescence and the sensitized-fluorescence spot test; the other three procedures are GC/MS procedures, one of which employs capillary GC/MS. The Level 2 Methods Manual provides GC and HPLC procedures to analyze PAH along with a HRGC/MS analysis procedure (80).

Both the PAH Assessment Document and the Level 2 Methods Manual employ the Level 1 clean-up procedure for isolation of PAH containing extracts prior to column chromatography and analysis (81). The problem with this procedure is the poor recovery characteristic of methylene chloride for high molecular weight PAH, e.g., benzo[a]pyrene, collected in the particulate catches. This problem is offset somewhat by the high front end temperature of the SASS train which drives much of the high molecular weight PAH to the XAD resin trap where it is easily recovered. Since the extent of this effect is not known at present, the analysis of high molecular weight PAH should be augmented by a second Soxhlet extraction after the methylene chloride extraction step. This re-extraction should employ a suitable extracting solvent, e.g., toluene or o-dichlorobenzene, with the second extract concentrated and added to the methylene chloride extract before HRGC/MS analysis.

The methods cited in this report are suggested procedures based on the best scientific judgment and await careful ruggedness testing and interlaboratory validation before they can be applied to stack samples with confidence.

DISCUSSIONS/RECOMMENDATIONS

PAH compounds are a complex class of compounds produced by combustion of fossil fuels such as coal or fuel oil. A well validated sampling and analysis procedure would involve the following:

- Collection in a SASS train or Method 5 collector which contain an XAD resin trap.
- Extraction, isolation, and concentration using Level 1 procedures.
- Additional extraction for PAH employing a separate particulate extraction solvent.
- Screening tests, e.g., the naphthalene-enhanced fluorescence spot test, should be used to identify PAH containing extracts.
- High resolution capillary gas chromatography with coupled low resolution mass spectrometry is recommended for compound identification and quantification if screening tests are positive.
- Development of a list of suspect PAH species based on known mutagenic/carcinogenic characteristics of individual compounds.

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SAMPLING AND ANALYSIS PROCEDURES FOR TRICHLOROETHYLENE

BACKGROUND

Trichloroethylene is a clear, colorless, noncorrosive, nonflammable sweet-smelling liquid (1). A summary of chemical and physical properties is shown in Table A-15. Trichloroethylene is produced primarily by chlorination and oxychlorination of ethylene (1). Although trichloroethylene is not highly reactive, it does slowly decompose upon exposure to light and water vapor to form hydrogen chloride and at elevated temperatures, chlorine (1).

TABLE A-15. CHEMICAL AND PHYSICAL PROPERTIES OF TRICHLOROETHYLENE

Property	Value
Formula	$ClCH = CCl_2$
Molecular weight	131.39
Physical state	Liquid
Melting point	-73°C
Boiling point	87°C
Density	1.465 (20°C)
Refractive Index	1.4773
Solubility	Very soluble in alcohol and ether; soluble in acetone; low solubility in water (0.1g/100 g H_2O at 25°C)

On contact with certain metals, open flames, or ultraviolet radiation, trichloroethylene decomposes to form phosgene and/or hydrogen chloride (1). It may also react with strong alkali to form the very toxic substance, dichloroacetylene, and other explosive mixtures (1).

Annual production of trichloroethylene in the United States is about 250,000 metric tons; approximately 80 percent of the trichloroethylene produced in the United States is consumed in the vapor degreasing of fabricated metal parts. In 1970, trichloroethylene accounted for 82 percent of all chlorinated solvents used in vapor degreasing. By 1976, that share had declined to 42 percent. A variety of miscellaneous applications included its use in adhesive and paint stripping formulations, as a low-temperature heat transfer medium, a nonflammable solvent carrier in industrial paint systems, a solvent for metal phosphatizing systems, and as a chain-transfer agent in the production of polyvinyl chloride.

Trichloroethylene should be stored in a cool, dry, and well ventilated area. Operations producing a high temperature and ultraviolet light such as open flames, unshielded resistance heating, and arc welding should be avoided where trichloroethylene vapors are present. Permissible airborne exposure is one hundred (100) parts of trichloroethylene vapor per million parts of air (100 ppm), time-weighted-average (TWA) for an 8-hour day with a ceiling limit of 150 ppm. No employees should be exposed to any eye or repeated skin contact with trichloroethylene.

SAMPLING AND ANALYSIS

Bursey, *et al.* (3) tested the application of capillary GC/MS computer techniques using Tenax-GC adsorbent to the identification and quantification of organic components in ambient air. This led to the determination of trichloroethylene, besides many other chlorinated hydrocarbons, in ambient air in Houston, Pasadena, Deer Park, Freeport, and La Porte, Texas areas. Quantitative information as well as identification of components can be extracted from the same analysis if the method of molar response (RMR) factors is used for the components of interest. This method requires information on the exact amount of standard added and the relationship of the RMR of the unknown to the standard.

The method of calculation is shown in the following equations:

$$\mathrm{RMR}_{\mathrm{unknown/standard}} = \frac{A_{\mathrm{un}}/\mathrm{moles}_{\mathrm{un}}}{A_{\mathrm{std}}/\mathrm{moles}_{\mathrm{std}}}$$

where A = peak area.

To determine RMR, a concentration of unknown and standard must be accurately known and the system response must be measured. The value must be determined for at least three independent analyses. The response in terms of area units is directly dependent upon the concentration of compound

$$\mathrm{RMR}_{\mathrm{un/std}} = \frac{A_{\mathrm{un}}/g_{\mathrm{un}}/\mathrm{GMW}_{\mathrm{un}}}{A_{\mathrm{std}}/g_{\mathrm{std}}/\mathrm{GMW}_{\mathrm{std}}}$$

down 7

where

where A = peak area,
g = sample weight, in grams, and
GMW = gram molecular weight of compound.

Thus, in any given sample,

$$g_{\mathrm{un}} = \frac{A_{\mathrm{un}} \cdot \mathrm{GMW}_{\mathrm{un}} \cdot g_{\mathrm{std}}}{A_{\mathrm{std}} \cdot \mathrm{GMW}_{\mathrm{std}} \cdot \mathrm{RMR}_{\mathrm{un/std}}}$$

Considerable effort remains to determine the overall applicability of the RMR method. For example, a question is to what extent a number for a response factor determined on one GC/MS system may be extrapolated to another. An obvious extension of the technique is to computerize the whole operation. If the computer is fed pertinent mass spectra, retention time windows, appropriate ions, and response factors, concentration of components could be obtained directly from the raw data without human intervention.

Brown and Purnell (4) investigated the adsorption characteristics of Tenax-GC, a polymer of 2,6-dipheny-p-phenylene oxide. The main advantages of this material over other porous polymers are a high temperature stability and hence low bleed thermal desorption and a relative insensitivity to the effects of water vapor. For trichloroethylene b.p. 87°C and desorption temperature 100°C, they found an extrapolated retention volume of 7.4 L; a safe sampling volume 3.7 L; a safe sampling volume per g of adsorbent 28 L for flow rates in the range 5 to 600 mL/min.

In the EPA procedure (5), an integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis using a flame ionization detector (FID). The range of this method is 0.1 to 200 ppm. The upper limit may be extended by extending the calibration range or diluting the samples. The avoidance of resolution interferences may require supplemental analytical techniques, e.g., analysis with a different column or GC/MS.

Battelle's Columbus Laboratories (6) measured trichloroethylene in the atmosphere near several industrial sites (Figure A-16). Ambient air was injected into a gas chromatograph, followed by detection of the emerging compounds with an electron capture detector (ECD). Estimated minimum detection levels were 1.0 ppb. GC analysis was performed by attaching the Teflon bag to the inlet of the sampling loop on a gas sampling valve.

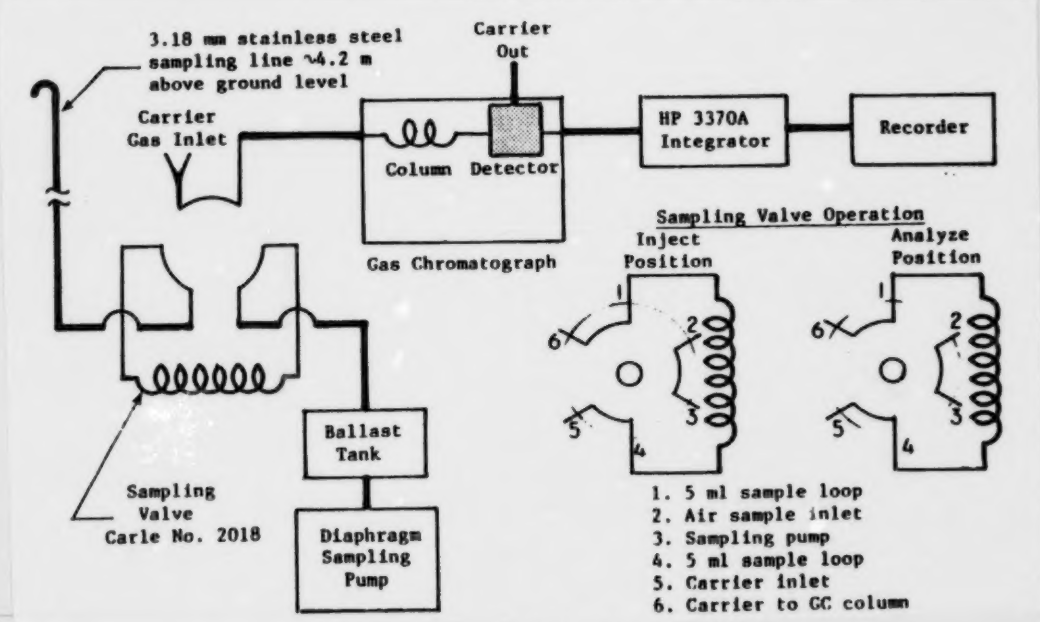
3.18 mm stainless steel sampling line ~4.2 m above ground level
Carrier Out
Carrier Gas Inlet
Column
Detector
Gas Chromatograph
HP 3370A Integrator
Recorder
Sampling Valve Operation
Inject Position
Analyze Position
1
2
3
4
5
6
Ballast Tank
Sampling Valve Carle No. 2018
Diaphragm Sampling Pump
1. 5 ml sample loop
2. Air sample inlet
3. Sampling pump
4. 5 ml sample loop
5. Carrier inlet
6. Carrier to GC column

Figure A-16. Schematic of GC/ECD ambient air analysis system for trichloroethylene.

DISCUSSION/RECOMMENDATIONS

The use of Tenax-GC polymer as an adsorbent for trichloroethylene is recommended because of high temperature stability, low bleed desorption and relative insensitivity to the effects of water vapor. An adsorbent tube consists of stainless-steel tubing (75 mm × 4.5 mm I.D.) and contains 0.13 ± 0.01 g of Tenax-GC (416 mesh), with adsorbent held in place with small plugs of silanized gas wool and stainless-steel gauze discs. The tube is sealed at each end with standard metal pipe fittings with polytetrafluoroethylene rings. Before use the tubes are conditioned under nitrogen for 16 hours.

Breakthrough on Tenax varies significantly with temperature. For the tube described herein, sampling should be conducted ideally at 50 mL/min, and in any event between 5 and 600 mL/min. Breakthrough also varies significantly with vapor concentration, although in the practical range for desorption, that is, below 100 ppm, deviations are toward larger breakthrough volumes and calculated safe sampling volumes still apply. Temperature markedly affects breakthrough with retention volumes being doubled for each 10° decrease in temperature. This is important in using information from extrapolated retention volumes and safe handling volumes for trichloroethylene sampled on Tenax-GC.

Tenax-GC is recommended for the analysis of trichloroethylene in a Level 2 study. For Level 1 efforts, EPA Method 106 with grab sampling is suggested. In this method, an integrated bag sample of stack gas containing halogenated organics is subjected to gas chromatographic analysis using a flame ionization detector. The range of this method is 0.1 to 200 ppm. Resolution interferences may be encountered in some sources but these interferences can be overcome by proper column selection and confirmation of analytical technique through gas chromatography/mass spectrometry. Major items in the apparatus for the above analysis are a probe made of stainless steel equipped with a glass wool plug to remove particulate matter; Teflon sample line; Tedlar or aluminized Mylar bags (100-L capacity); charcoal tube to prevent the admission of halogenated organics to the atmosphere in the vicinity of the sampler; and a gas chromatograph equipped with an FID detector, potentiometric strip chart recorder, 1.0 to 2.0 mL sampling loop in an automatic sample valve, and a chromatographic column of stainless steel 3.05 m by 3.2 mm containing 20% (W/W) SP-2100/0.1% (W/W) Carbowax 1500 on 100/120 Supelcoport. Other columns may be used that give adequate resolution defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak.

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SAMPLING AND ANALYSIS PROCEDURES FOR VINYL CHLORIDE AND VINYLIDENE CHLORIDE

BACKGROUND

Vinyl chloride (VC) is an important industrial chemical capable of readily polymerizing in the presence of ultraviolet radiation or peroxides to homopolymer, polyvinylchloride (PVC). A list of some chemical and physical properties of VC is given in Table A-16. The world production of VC in 1971 was approximately seven billion kilograms, the U.S. producing about two billion kilograms of the total (1). The total U.S. capacity for ethylene dichloride, the predominant raw material for VC manufacture, was 5.6 billion kilograms in 1974 (2). VC is usually manufactured by the direct chlorination of ethylene followed by dehydrochlorination and is produced in far smaller amounts by hydrochlorination of acetylene.

Vinyl chloride is implicated in reported incidences of angiosarcoma among workers exposed to high levels while cleaning reactor vessels (3). Recent research has shown that VC inhalation produces angiosarcoma of the liver and other organs in rats and mice (4) with carcinogenic effects measured at levels as low as 50 ppm (5). An occupational standard of 1 ppm 8-hour TWA exposure with a limit of 5 ppm for a 15 minute short-term exposure provides some protection.

Vinylidene chloride, 1,1-dichloroethylene, is commercially produced by the dehydrochlorination of trichloroethane. Some chemical and physical properties of vinylidene chloride are listed in Table A-17. Vinylidene chloride is widely used to produce a clear film for food wrapping and as an intermediate in the production of 1,1,1-trichloroethylene. Although the large data base on carcinogenicity and mutagenicity of vinylidene chloride is often conflicting, an excellent review has been written by Fishbein (5).

TABLE A-16. CHEMICAL AND PHYSICAL PROPERTIES OF VINYL CHLORIDE

Property	Value
Formula	$CH_2=CHCl$
Molecular weight	62.50
Physical state	Gas
Melting point	-154°C
Boiling point	-13°C
Density	0.9106 (20°C)
Refractive index	1.3700
Solubility	Soluble in alcohol; slightly soluble in water; very soluble in ether

TABLE A-17. CHEMICAL AND PHYSICAL PROPERTIES OF VINYLIDENE CHLORIDE

Property	Value
Formula	$CH_2 = CCl_2$
Molecular weight	96.94
Physical state	Liquid
Melting point	−122°C
Boiling point	37°C
Density	1.218 (20°C)
Refractive index	1.249
Solubility	Soluble in alcohol, acetone, and benzene; insoluble in water

As part of Section 112 of the Clean Air Act, the EPA added vinyl chloride to the list of hazardous air pollutants and promulgated a national emission standard for plants producing VC, PVC, and ethylene dichloride (6-8). In a more recent action, the U.S. Environmental Protection Agency proposed a reduction in the national emission standard for VC from 10 to 5 ppm (9).

SAMPLING AND ANALYSIS

Sampling for vinyl chloride usually involves either a grab sample or a scrubbing device using a solid sorbent. VC has been collected in Tedlar bags or stainless steel canisters (10). The Tedlar bags showed less than 10 percent loss of VC although storage in the presence of NO_2 produces reactions when the bag is exposed to sunlight. A test method for measuring vinyl chloride in stationary sources, denoted Method 106, has been published in the *Federal Register* (11,12). This procedure involves collecting an integrated Tedlar bag sample of stack gas using a stainless steel probe with connecting tubing of glass or Teflon. The Tedlar (or aluminized Mylar) bag is held in a rigid, sealed container that has two gas connections, one into the bag and one to the space surrounding the bag. The bag is filled by reducing pressure to the outside connector so the sample bag fills in much the same way the human diaphragm operates to fill the lungs. The Tedlar bag method is illustrated in Figure A-17. Method 106 has been tested in a validation study (13) and by a multilaboratory test (14).

The validation study showed that field samples of VC were stable in Tedlar bags for longer than one week but aluminized Mylar could only hold a representative sample for 24 hours. The collaborative test of Method 106 performed by ten participating laboratories showed a standard deviation of 0.39 ppm (1.01 mg/m^3) for convenient sampling of the vent from a carbon bed, VC adsorber. Recently the integrated-bag sampling train has been proposed as a standard procedure for sampling other halogenated organics in stationary sources including carbon tetrachloride, ethylene dichloride, perchloroethylene, and trichloroethylene (15).

Solid scrubbers have been used for VC collection with primary emphasis on charcoal collectors subjected to solvent elution after sample collection. Charcoal has a limited capacity

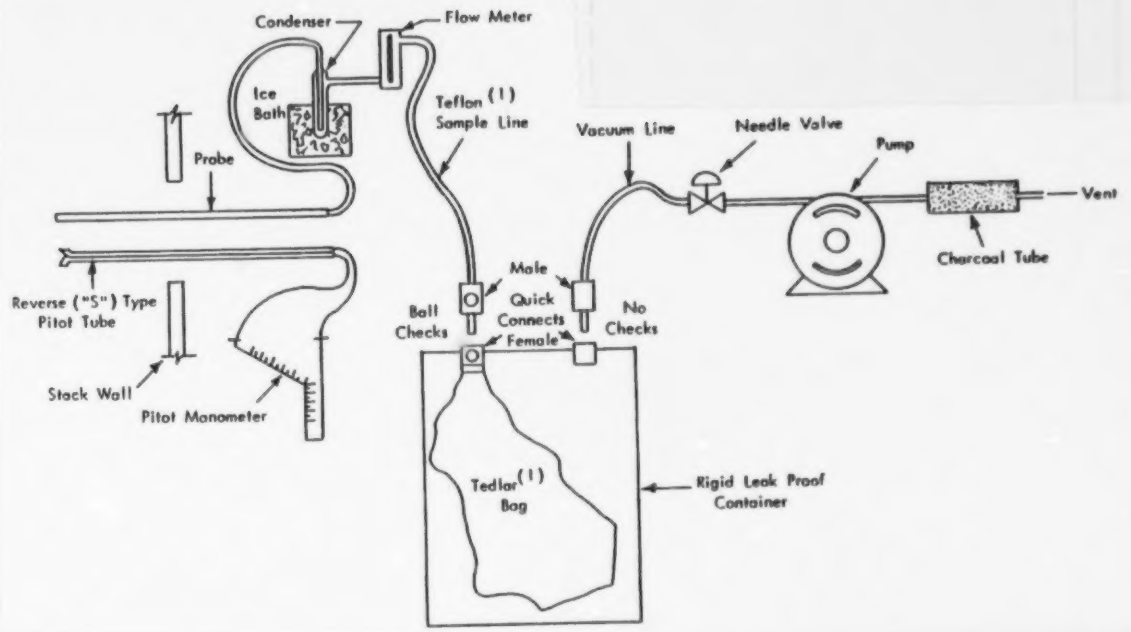
Condenser
Flow Meter
Ice Bath
Teflon (1) Sample Line
Vacuum Line
Needle Valve
Pump
Vent
Probe
Charcoal Tube
Male
Reverse ("S") Type Pitot Tube
Ball Checks
Quick Connects
Female
No Checks
Stack Wall
Pitot Manometer
Tedlar (1) Bag
Rigid Leak Proof Container

Figure A-17. Integrated bag sampling train.

for VC and is subject to poisoning by the stack gases normally found in coal and fuel oil combustion. Charcoal has received much attention as a medium for collecting VC after it was chosen as the NIOSH standard procedure for workplace monitoring (16). In this procedure, an air sample is drawn through the charcoal tube and the collected VC is recovered by CS_2 extraction. The CS_2 is then subjected to GC/FID analysis in which the solvent, carbon disulfide, is not measured by the flame ionization detector. The NIOSH procedure has a stated sensitivity of 200 pg VC from a 5-liter sample. The method has a published range of 8 mg/m^3 (3 ppb) to 5.2 mg/m^3 (2 ppm) with a stated precision of 0.08 mg/m^3 at a concentration of 7 mg/m^3 (2.7 ppm). Miller, *et al.* have employed this technique for atmospheric sampling and claim a sensitivity of 5 ppb (17).

Hill and co-workers (18) have investigated 20 different solid sorbents and found coconut charcoal to be the best with Molecular Sieve (5A), Carbopak B and Carbosieve B having good collection behavior for high concentrations of VC and Dow Carbon XE417SL having highest capacity for low concentrations. McClenney, *et al.* (19) used activated charcoal and the combination of gas chromatography and a chemiluminescence detector to achieve 50 pptr sensitivity for ambient air VC analysis. Phillip West and colleagues (20) have proposed a variant on pulling the gas sample through charcoal. They have developed a silicon membrane device that allows VC to permeate into a charcoal chamber which is removed for analysis of the time-weighted-average concentration of VC in industrial environments.

Several other solid scrubbers have been proposed for VC collection, including porous polyaromatic polymer beads (21), Porapak Q (22), and Carbowax 500 coated support under cryogenic conditions (23).

Use of the charcoal sampling method for stationary source analysis was tested in a parallel study of Method 106 (see reference 14, page 49, for a summary of the method). The authors found charcoal to be a simpler sampling technique but the analysis was more difficult and routinely yielded data 20 percent lower than Method 106. Thus, Method 106 is preferred to charcoal tube sampling for stack gas analysis.

The usual analysis procedure for vinyl chloride involves elution by gas chromatography with flame ionization or electron capture (EC) detection, although GC with mass spectrometric detection has been used to confirm the presence of VC (24,25). Table A-18 gives some of the stationary phases and detectors which have been applied to the analysis of vinyl chloride.

Several detectors have been suggested for vinyl chloride. As shown in Table A-19, they show variable sensitivities for VC detection.

TABLE A-18. STATIONARY PHASES AND DETECTORS PROPOSED FOR VINYL CHLORIDE ANALYSIS

GC Stationary Phase	Detector	Reference(s)
Porapak Q	FID	(26, 27)
DC 550	FID	(28)
$AgNO_3$/ethylene glycol	FID	(29)
Diisodecyl phthalate/ ethylene glycol	FID	(30)
SE-30	FID	(31)
Carbowax 4000	FID	(32)
Chromosorb 102	FID, ECD	(12, 14, 33)
SF-96 on Chromosorb P	FID	(12, 14)
0.4% Carbowax 1540 on Carbopak A	FID	(34)
0.19% picric acid on Carbopak C	FID	(34)
Porapak C	EDC (with N_2O)	(35)

TABLE A-19. SENSITIVITY OF SELECTED DETECTORS USED FOR VINYL CHLORIDE DETECTION (12,35,36,37)

Detector	Sensitivity (g)
Thermal Conductivity	2×10^{-6}
Chemiluminescence	20×10^{-4}
Argon Ionization	1.9×10^{-9}
FID	2.2×10^{-9}
ECD	2.3×10^{-9}
ECD (with N_2O)	1.4×10^{-12}

Although the flame ionization detector is specified for Method 106 a new detector, N_2O enhanced ECD, offers 10^3 greater sensitivity for trace level analysis of VC.

An ultralow-concentration technique has been reported by Dagmar Cronn and co-workers at the University of Washington who used liquid oxygen to trap an ambient air sample and performed parts-per-trillion analysis using GC/ECD (38).

DISCUSSIONS/RECOMMENDATIONS

Of the available sampling procedures for vinyl chloride, grab sampling by means of Tedlar bags and charcoal adsorption appear to have the best characteristics for stationary source sampling for vinyl chloride. These methods are compared in Table A-20.

TABLE A-20. COMPARISON OF VINYL CHLORIDE SAMPLING METHODS

Method	Advantages	Disadvantages
Tedlar Bag	Integrated sample 100 liters collected	Light sensitivity One-week storage limitation Bulky sampling apparatus
Charcoal Trap	Easy to handle Easy to ship Simple sampling	Low capacity for vinyl chloride Complicated analysis Potential for poisoning from stack gas

The recommended procedure for analyzing vinyl chloride is Method 106 which has undergone validation for stationary source sampling. The SF-96 Chromosorb P, GC column was preferred to Chromosorb 102 in the Method 106 validation study. An alternate procedure has been proposed in the Level 2 Methods Manual which employs GC/MS with a column material of 0.2 percent Carbowax 1500 on 80/100 mesh Carbopak C (39). Vinyl chloride elutes at 0.8 minute under the conditions of the Level 2 method which was validated by purge and trap elution.

The Level 2 procedure, cited for applicability to vinyl chloride, has also been demonstrated for vinylidene chloride, showing a retention time of 3 minutes on the proposed Carbowax 1500 C column and good separation from the 26 alkylhalides tested. Although the Level 2 procedure recommends GC/MS, Hall Electrolytic Conductivity and electron capture are suggested as alternate detectors to measure both vinyl chloride and vinylidene chloride. A sensitivity of 10 pg is cited for the electron capture detector which corresponds to a minimum detectable quantity of 2 mg/m^3 for an injection volume of 5 mL.

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SAMPLING AND ANALYSIS PROCEDURES FOR ARSENIC

BACKGROUND

Arsenic is not an abundant element; it is found at approximately 5 μg/g concentration in the earth's crust. However, it is so widely distributed that traces can be found almost everywhere. It is also present in sea water (10-100 ppb) and is concentrated in aquatic creatures like shrimp (1). It is commonly found as sulfide, arsenide, arsenite, or arsenate. Occasional deposits of elemental arsenic are found, but none are commercially important (2).

Arsenic is mainly produced by smelters processing arsenic containing ores. The major sources of arsenic in air are exhaust fumes of smelting lead, copper, and gold ores, burning of cotton trash during cotton ginning, coal combustion, and emissions from insecticide, herbicide, and pesticide industries. The physical/chemical properties and toxicity of arsenic compounds are summarized in Table B-1 (3).

SAMPLING METHODS

The most commonly found arsenic compound in stationary source emissions is arsenic trioxide (As_2O_3) which sublimes at 193°C. Arsenic metal, arsenic sulfides, arsine, arsenic (V) oxide (in the presence of reducing agents) and organic arsenates are all converted by heat and oxygen to arsenic trioxide. Frequently very low levels of arsine emitted during metal pickling, soldering, etching, and plating processes are detected in the air.

Since arsenic trioxide can be easily suspended in air as small particles, a sampling train with particulate collectors will normally recover most of it. In the past, fabric filters were used to remove arsenic particulate matter from flue gases. More recently they were replaced by wet vacuum pumps that were found to be 100 percent effective (4).

EPA Method 5 as modified September 19, 1977 (5) was used to sample particulate matter such as arsenic and arsenic compounds by withdrawing the sample isokinetically into the sampling train. The train consisted of the following components: a stainless steel or glass probe nozzle with an appropriate liner (e.g., borosilicate or quartz glass) capable of maintaining a gas temperature at the exit of 120°C ± 14°C; an S type pitot tube; a differential pressure gauge; a borosilicate glass filter holder; a filter heating system capable of maintaining a temperature of 120°C ± 14°C during sampling; and a condenser system consisting of four impingers for determining the stack gas moisture content. The first and second impingers are of the modified Greenberg-Smith design and contain known amounts of water; the third is the same design but empty; and the fourth is of the same design but with no modification and is filled with a desiccant (silica gel, calcium sulfate, or any other appropriate material). The system also includes a metering system consisting of a vacuum gauge, leak-free pump, thermometer, volume measuring gas meter, barometer, and gas density determination equipment.

Flegal, *et al.* (6,7) designed a system to sample trace amounts of arsenic in flue gas streams. This system is based on a standard Aerotherm high volume stack sampler (HVSS) but was modified in three areas: (1) the probe was lined with an inner removable liner made of Kapton polyimide film to prevent stainless steel elements from contaminating the particulate catch, (2) Gelman Spectrograde type A glass fiber filter was used as the filtering medium, and (3) a special oxidative impinger system was developed to sample vaporous elements such as arsenic,

TABLE B-1. PROPERTIES AND TOXICITY OF ARSENIC COMPOUNDS

Compound	Properties	Toxicity
Arsenic trioxide (White arsenic) As_2O_3	m.p. 313°C b.p. 465°C Sublimes at 193°C d. 3.74 g/cm^3 Soluble in water, Alkali, HCl	Most forms of arsenic are highly toxic. Acute symptoms following ingestion relate to irritation of the gastro-intestinal tract: nausea, vomiting, diarrhea which can progress to shock and death. Chronic poisoning can result in exfoliation and pigmentation of skin, herpes, polyneuritis, altered hematopoiesis, degeneration of liver and kidneys. LD_{50} for rats 13,000 g/kg; for man 0.0-0.5 g; chronic under 0.1 g; phytotoxicity: very toxic to plants.
Arsenic disulfide As_2S_2	m.p. 320°C b.p. 565°C d. 3.519(2) g/cm^3 Soluble in K_2S, $NaHCO_3$	Most forms of arsenic are highly toxic; see arsenic trioxide
Arsenic	m.p. 617°C (28 atm) Sublimes at 613°C d. 5.7314 g/cm^3 soluble in HNO_3	Toxic
Arsenic hemiselenide As_2Se_3	Decomposes; soluble in alkali; decomposes in hot water	Same as arsenic trioxide
Arsenic pentafluoride AsF_5	m.p. −79.8°C; b.p. −53.2°C; soluble in alk, alcohol, ether and benzene	Same as arsenic trioxide; also, external contact—liquid or vapor—causes severe irritation of the eyes
Arsenic pentoxide As_2O_5	m.p. 315°C d. 4.32 g/cm^3 soluble in water, alcohol and alkaline	Poisonous: keep well closed. LD i.v. in rabbits 8,000 g/kg

TABLE B-1. (Continued)

Compound	Properties	Toxicity
Arsenic tribromide $AsBr_3$	m.p. 32.8°C b.p. 221°C d. 3.5425 g/cm^3 Soluble in HCl, HBr and CS_2	See arsenic trioxide; intensely poisonous; also highly irritating to skin, eyes, mucous membranes, respiratory tract
Arsenic trichloride $AsCl_3$	m.p. −8.5°C b.p. 130.21°C Soluble in HBr, PCl_3, alcohol and ether	Extremely toxic; readily liberates hydrochloric acid, which is a strong irritant; also see arsenic trioxide
Arsenic trifluoride AsF_3	m.p. −8.5°C b.p. 63°C d. 2.67 g/cm^3 Decomposes in water Soluble in alcohol, ether, benzene and NH_4OH	Extremely toxic; see arsenic trioxide
Arsenic triiodide AsI_3	m.p. 146.9°C b.p. 403°C d. 4.39 g/cm^3 Soluble in H_2O, CS_2, alcohol, ether, benzene, $CHCl_3$	See arsenic trioxide
Arsenic trisulfide As_2S_3	m.p. 300-325°C b.p. 707°C d. 3.43 g/cm^3 Soluble in alcohol, alkali, alkali carbon	See arsenic trioxide
Arsine AsH_3	m.p. -117°C b.p. 55°C Soluble in water, chloroform and benzene	Injurious in 1:20,000 dilution; a few inhalations may be fatal; death from anoxia or pulmonary edema; hemolytic anemia in nonfatal cases
Calcium arsenate $Ca_3(AsO_4)_2$	Powder	See arsenic trioxide; poisonous; LD_{50} 35-100 mg/kg for various animals; phytotoxicity: causes leaf and fruit damage to stone fruit trees

TABLE B-1. (Continued)

Compound	Properties	Toxicity
Lead arsenate $PbHAsO_4$	White heavy powder; decomposes above 280°C	Poisonous; LD$_{50}$ orally in rats 80,000 g/kg; LD$_{50}$ in animals 10,000-50,000 g/kg; man 0.1-0.5 g
Potassium arsenate KH_2AsO_4	Decomposes	Poisonous
Cacodylic acid $(CH_3)As(O)OH$	m.p. 195-196°C	Poisonous; 1.0 g/kg LD s.c. for dogs
Sodium arsenate dibasic Na_2HAsO_4	m.p. 57°C	Poisonous but less so than arsenite
Sodium arsenite $NaAsO_2$		Very poisonous; keep well closed; see arsenic trioxide

mercury, selenium, and antimony. The oxidative system consisted of four impingers: one impinger with 3M H_2O_2, two impingers with 0.2M $(NH_4)_2 S_2O_8$ plus 0.02M $AgNO_3$, and a fourth impinger with Drierite. The impinger nozzles were coated with Teflon to prevent corrosion of the stainless steel components due to the oxidative solutions.

This system is designed to operate in a flue gas stream at temperatures up to 450°C. The sampling rate reaches 90 L/min (3 cfm). This system is primarily designed for trace material sampling, but can also be used to collect information on mass loadings. Following are some of the limitations: while the Kapton lined probe can operate up to 450°C, Teflon gaskets and coated hardware are not compatible with temperatures much above 270°C. The Aerotherm system is also heavier and larger than low volume Method 5 type samplers. Cleaning the cooling coils can be difficult and time consuming, and they also show potential for corrosion or impinger sample contamination. While manufacturer specifications indicate that a sampling rate of 180 L/min (6 cfm) is possible, present field sampling has demonstrated that a sampling rate of 90 L/min (3 cfm) is possible with the present configuration.

The same authors (7) also developed a similar system for sampling vaporous trace elements like arsine in flue gases. It consists of four impingers, commonly found in a Method 5 train, filled with 3M H_2O_2 in the first impinger, 0.2M $(NH_4)_2 S_2O_8$ plus 0.02M $AgNO_3$ in the next two impingers, and Drierite in the last impinger. The 3M H_2O_2 passes Hg vapor but removes the SO_2 to prevent depletion of the Ag catalyzed $(NH_4)_2 S_2O_8$ solution. The persulfate solution is specifically designed to remove Hg, but will collect any Se, Sb, As, or Pb that passes through the peroxide impinger. In all cases, the volatile species are oxidized in the H_2O_2 or $(NH_4)_2 S_2O_8$ and are effectively scrubbed from the gas stream. This oxidative system was designed to operate in the modified Aerotherm system (HVVS), but can be used in any commercially available system employing glass or plastic impingers.

The EPA Level 1 Source Assessment Sampling (SASS) train (8) has been by far the most widely used system for sampling inorganics including arsenic and its compounds. It is mainly designed to collect large quantities of particulate matter, size classified in the range of 10 μ, 3-10 μ, 1-3 μ and <1 μ, as well as inorganic volatile species that can be liquid or solid adsorbed. The sampling train consists mainly of a probe, which enters an oven module containing three cyclones and a filter designed to give the particulate delineation from <1-10 μ, an impinger series containing $(HN_4)_2 S_2O_8$, $AgNO_3$, high purity water and H_2O_2, and a high volume vacuum pump. It is designed to operate up to 205°C in flue gas streams and to operate unattended even when isokinetic sampling conditions cannot be met.

ANALYTICAL PROCEDURES

Analysis for the final sample of arsenic from a sampling train can be accomplished at the μg level using several techniques. The main approach to quantitative analysis of arsenic is to convert all arsenic compounds to arsine. The arsine is then detected using several methods, such as reaction with copper foil (Reinsch's method) or silver nitrate or mercuric chloride (Gutzeit's test) or simply to heat it and convert it to metallic arsenic (March's test) (9,10).

A general method for arsenic analysis in both air and liquid matrices is the combined arsine generation/colorimetric method (11,12,13). The samples are ashed in nitric, perchloric, and sulfuric acid to destroy any organic material that might be present, the ash is treated with ammonium oxalate and taken to fumes of SO_3 to remove the last traces of nitric acid. Arsine is then generated by using KI,HCl and $SnCl_2$, and metallic zinc. Arsine is absorbed by a solution of pyridine silver diethyldithiocarbamate and adsorbance is measured at 560 nm wavelenth. This method is sensitive to 0.01 mg/m^3 air for a 30-liter sample. As with similar colorimetric methods, interferences, lack of reproducibility, and accuracy are drawbacks for the use of such a method.

Reaction kinetics combined with arsine generation from arsenic compounds is a reliable and relatively easy technique to use as demonstrated by Burgess, *et al.* (14) and others (15,16,17,18). Particulate material containing arsenic is collected on a membrane filter in a sampling train. The filter and trapped particulate material are wet-ashed with a mixture of nitric and sulfuric acids or dry-ashed in low temperature asher. The nitric acid is removed from the wet-ashed sample, or the dry-ashed sample is dissolved in sulfuric acid. The resulting As (V) is reduced to As (III) with an acidic solution of potassium iodide and sodium formate. The chemically reduced sample is neutralized and As (III) is determined by the kinetics of a catalytic reaction. In the catalytic reaction, As (III) promotes the osmium [Os (VIII)] catalysis of the oxidation of iodide to iodine by bromate. The rate of iodine production is proportional to the concentration of As (III) and is determined after a four-minute reaction time by measurement of the absorbence at 580 nm with starch as an indicator. The method has a sensitivity of 0.1 mg/m^3 for a 25-liter air sample.

Anodic stripping voltammetry (ASV) (19,20) is used in combination with the ashing/hydride generation procedure. A composite gold-graphite electrode (CGGE) is used. The method is sensitive to 0.0005 mg/m^3 in a 100-liter air sample. Relative variance of the method is ±10 percent.

Neutron activation analysis is a fast, reliable, and sensitive technique (detection limit is 0.005 μg) (21) for arsenic elemental analysis; however, it requires a neutron generator that limits its availability.

X-ray fluorescence (22) can also be used to detect arsenic at 0.01 μg/cm^2 levels. The speed and general applicability of this technique are quite advantageous.

Ion chromatography (IC) was applied successfully to the analysis of arsenate in the extract of particulate collected from a copper smelter by means of a SASS train (23). IC when applied to artificial arsenic samples was found to have an accuracy of 99% versus 97% for the silver diethylidithiocarbamate method and an average standard deviation of 17.4 for an average area counts of 2,220 for a concentration range of 5.2-12.8 μg/mL of the oxo anion.

Inductively coupled plasma-optical emission spectroscopy (ICAP) (24,25) is becoming a widely used technique for arsenic analysis when multielement determinations are required. Detection limits of 53 μg/L are achieved. The relative standard deviations determined for three concentrations, 200, 22, and 60 μg/L, were 7.5, 23, and 17 percent, respectively.

Atomic absorption spectrophotometry (AAS) (26,27,28) combined with the hydride generation step is by far the most widely used technique and the method of choice for analyzing sampling train collectors. The procedure entails the reduction and conversion of arsenic and its compounds to the hydride in an acid solution with either $SnCl_2$ and metallic zinc or $NaBH_4$ (29,30). The generated hydride is swept in a stream of argon into an argon-hydrogen flame in an atomic absorption spectrophotometer using the 193.7 nm wavelength. The detection limit of hydride generation AAS was reported to be 0.2 μg/L with an accurate concentration range of 0.02-2 μg in solution.

DISCUSSION/RECOMMENDATIONS

Table B-2 summarizes the highlights of the available sampling procedures. The Flegal, *et al.* (6,7) sampling train described above is recommended for collecting arsenic emissions from stationary sources combined with the hydride generation/AAS detection method because:

- It has the advantages of the SASS train but is less complicated.
- It allows for trapping volatile particulate, and possibly organo-arsenic compounds.

TABLE B-2. ADVANTAGES AND DISADVANTAGES OF ARSENIC SAMPLING AND ANALYSIS PROCEDURES

Procedure	Advantages	Disadvantages
EPA Method 5 Sampling Train	Simple train, sufficient for collecting particulate arsenic Combined with AAS/hydride generation analytical procedure provides a sensitive approach Easy to modify Available commercially	Does not collect volatile components efficiently and without modification Not adequate for very low levels because of sample size Impinger system not originally designed for metals collection Complex and expensive to operate
EPA SASS Train	Collects both particulate and volatile arsenic compound in the cyclone/filter and impinger systems, respectively Provides low detection limits by allowing for large sample collection When combined with the hydride generation/AAS analytical method, it provides an adequate approach Commercially available When combined with the hydride generation/AAS analytical method, it provides an adequate approach	Difficult to clean The stainless steel parts corrode when exposed to acidic fumes Difficult to modify

TABLE B-2 (Continued)

Procedure	Advantages	Disadvantages
Modified Aerotherm HVSS Sampling System by Flegal, *et al.*	Designed specifically for arsenic and similar metals sampling Probe in line with Kapton polyimide to prevent stainless steel corrosion Has suitable impinger system for arsenic compounds collection The impinger nozzles are coated with Teflon to prevent corrosion Operates under relatively high temperature and pressure conditions	Not available commercially Difficult to clean Teflon parts in system limits its applicability to 270°C as an upper limit
Hydride Generation/ AAS Analysis	Combines the hydride/AAS technique which minimizes interferences When combined with the digestion method using nitric/perchloric/ sulfuric acid mixture, it can minimize inaccuracies due to resistance of organo arsenic compounds to hydride generation Provides the lowest detection limits and the highest accuracy of all the above-mentioned alternative methods	Procedure is lengthy Requires specialized equipment

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SAMPLING AND ANALYSIS PROCEDURES FOR BERYLLIUM

BACKGROUND

Beryllium is not an abundant element existing in small quantities (0.006 percent) (1) in the earth's crust. Beryllium is found most commonly in the oxide form. The physical/chemical properties and the toxicity of beryllium and beryllium compounds are summarized in Table B-3.

TABLE B-3. PROPERTIES AND TOXICITY OF BERYLLIUM AND SOME BERYLLIUM COMPOUNDS

Compound	Properties	Toxicity
Beryllium (Be)	m.p. 1,284-1,300°C b.p. 2,970°C Gray metal with stiffness exceeding that of steel. Stable metal, but tarnishes slightly at room temperature (dry air and pure oxygen).	Death may result from short exposure to incredibly low concentrations of the element and salts. Concomitant exposure to acid fumes (hydroflouric) may increase toxic effects. Contact dermatitis, chemical conjunctivitis, corneal burns, nonhealing ulceration at site of injury, subcutaneous nodules may occur following exposure. Acute: pneumonitis may result from single exposure to beryllium and occasionally is fatal. Chronic: pulmonary granulomatous disease may appear in 3 months to 15 years, often after short exposure to low concentration. Uncertainty as to complete recovery. Death rate about 25 percent
Beryllium bromide ($BeBr_2$)	Crystals m.p. 488°C Sublimes at 473°C b.p. 520°C	
Beryllium carbide (Be_2C)	Decomposes above 2,100°C Brick-red or yellow-red octahedra	
Beryllium chloride ($BeCl_2$)	White to faintly yellow crystals m.p. 405°C b.p. 488°C	

TABLE B-3. (Continued)

Compound	Properties	Toxicity
Beryllium hydride (BeH_2)	White solid	
Beryllium hydroxide ($Be(OH)_2$)	Amorphous powder or crystals	
Beryllium iodide (BeI_2)	Needles m.p. 480°C b.p. 488°C	
Beryllium nitrate ($Be(NO_3)_2$)	White to slightly yellow crystals m.p. 60°C	
Beryllium oxide (BeO)	Light amorphous powder m.p. 2,530°C	
Beryllium potassium sulfate ($K_2Be(SO_4)_2$)	Brilliant crystals Soluble in water	
Beryllium sulfate ($BeSo_4$)	Crystals at about 100°C; loses $2H_2O$	LD_{50} in mice: 500 μg/kg Human toxicity: see beryllium.

The major sources of beryllium in the atmosphere are industrial processing plants engaged in the extraction, refining, machining, and alloying of the metal. Coal combustion is also a source of beryllium emissions. Because beryllium is among the most toxic and hazardous of the nonradioactive substances being used in industry, special sampling trains were designed for sampling beryllium in the atmosphere.

SAMPLING METHODS

A high volume sampler that draws air through a filter (cellulose fiber, cellulose ester, or fiberglass) for an appropriate period of time was designed (2). Flow rate of 1.5 to 1.7 m^3/min for a period of 24 hours is normally sufficient for sampling beryllium at 0.002 $\mu g/m^3$.

EPA Method 104 (3) is the most commonly used sampling train for measuring beryllium emissions. Stack gas is isokinetically sampled from the stationary source and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry. The main components in the train are: a stainless steel or glass nozzle with sharp, tapered leading edge; a sheathed Pyrex glass probe with a heating system to maintain proper temperature during sampling; a type S pitot tube to monitor gas velocity; a filter (Millipore AA and Whatman 41) and filter holder with a heating system; four Greenburg-Smith impingers with the first, third, and fourth modified by replacing the tip with half-inch i.d. glass tube extending to one-half inch from the bottom of the flask; a metering system; barometer; stack conditions measuring system; differential pressure gauge; temperature gauge; pressure gauge; and moisture determination wet and dry bulb thermometer.

Peters, *et al.* (4) evaluated EPA Method 104 by sampling simultaneously with two duplicate trains. The EPA specified clean-up procedure was followed strictly for one train, with the impinger solutions and the probe washes from the other train kept separate to provide an approximation of the distribution of Be within the trains. Most of the beryllium was found on the filter with some indication that some beryllium was present in the impingers (~17 percent of total amount measured). The recovery of beryllium using this method was found to be 116-123 percent from replicate precision and accuracy runs. However, 100 percent recovery was obtained when Method 104 without modification was used. The modification was the use of a quartz fiber filter and 0.1N HNO_3 impinger and wash solutions.

EPA Method 5 as modified effective September 19, 1977 (5) was used to sample particulate matter such as beryllium particulate by withdrawing the sample isokinetically into the sampling train. The train consisted of the following components: a stainless steel or glass probe nozzle with an appropriate liner (e.g., borosilicate or quartz glass) capable of maintaining a gas temperature of 120°C ± 14°C at the exit, an S type pitot tube; a differential pressure gauge; a borosilicate glass filter holder; a filter heating system capable of maintaining a temperature of 120°C ± 14°C during sampling; and a condenser system consisting of four impingers, two of which are of the modified Greenberg-Smith design and contain known amounts of water, the third is the same design, but empty, and the fourth is of the same design but with no modification and is filled with a desiccant (silica gel, calcium sulfate or any other appropriate material). The train also includes a metering system consisting of a vacuum gauge, leak-free pump, thermometer, a volume measuring gas meter, a barometer, and gas density determination equipment. The sample is recovered from the system by washing the nozzle and probe liner with acetone and combining the wash eventually with the particulate matter collected on the filter and filter holder. Since this method involves gravimetric analysis of particulate content, no further specific analysis is carried out.

Hamersma, *et al.* (6) developed a similar sampling train for high pressure gas sampling for gasifier outputs that included a pressure reduction system, a modified ASTM liquid sampling probe (9), a water-condensing impinger, and a series of three impingers containing 3 M H_2O_2, 0.2M $(NH_4)_2S_2O_8$, and 0.02M $AgNO_3$ for trace metal (cadmium) absorption, and a fourth impinger containing Drierite. This method is applicable for sampling outputs with temperatures of up to 500°C and pressures of no greater than 300 psig under isokinetic sampling conditions. Sampling rate is 2-10 m^3 of gas over a 104-hour period.

EPA Level 1 Source Assessment Sampling (SASS) train (7) has been by far the most widely used system for sampling inorganics including beryllium and compounds. This system is mainly designed to collect large quantities of particulate matter, size classified in the range of 10 μ, 3-10 μ, 1-3 μ and <1 μ, as well as inorganic volatile species that can be liquid absorbed. The sampling train consists mainly of a probe, which enters an oven module containing three cyclones and a filter designed to give the particulate delineation for <1-10 μ, an impinger series containing $(NH_4)_2S_2O_8$, $AgNO_3$, high purity water and H_2O_2, and a high volume vacuum pump. It is designed to operate up to 205°C in flue gas streams, and to operate unattended if the degree of nonisokinetic sampling level varies widely.

Flegal, *et al.* (8) designed a system to sample flue gas streams for trace inorganic materials based on a standard Aerotherm high volume stack sampler (HVSS) with the following modifications: (1) the probe was lined with an inner removable liner made of Kapton polyimide film to prevent contamination from stainless steel components, (2) a Gelman Spectrograde type A glass fiber filter was used as the filtering medium, and (3) a special oxidative impinger system consisting of four impingers: one impinger with $3MH_2O_2$, two impingers with $0.2M\ (NH_4)_2S_2O_8$ plus $0.2M\ AgNO_3$, and a fourth with Drierite. The impinger nozzles are Teflon coated to prevent corrosion of the stainless steel components due to the oxidative solutions. This system is designed to operate in a flue gas stream at temperatures up to 450°C with a sampling rate of up to 90 L/min.

ANALYTICAL PROCEDURES

Cholak, *et al.* (9) used the Morin fluorimetric method to analyze for beryllium in air. The beryllium particulate is removed from the filter, and processed to form an alkaline solution to which the fluorescent morin solution ($C_{15}H_{10}O_7\ H_2O$) is added. Reduction in fluorescence is proportional to the amount of beryllium present in solution. The lower detection limit of the method is 0.01 g of beryllium (9) or 0.00002 μg/mL (10).

Keenan, *et al.* (10) determined beryllium in air using the Zenia Method. The method involves removing the beryllium particulate from the filter paper of the sampling train, adding the Zenia solution (p-nitrobenzeneresorcinol), and measuring the absorbance of the reddish-brown solution spectrophotometrically.

A spectrographic method suitable for measuring trace quantities (0.003 μg) of beryllium in the atmosphere involves the addition of a thallium standard to the beryllium-zenia solution produced as in the above-mentioned colorimetric method. The solution is subjected to an electric arc after being concentrated and photographs of the spectral lines are recorded. The intensities of the beryllium line at 234.8 nm and the thallium line at 237.9 nm are measured. Improvement in sensitivity was accomplished by McCloskey (11) by using aluminum reagent in place of the Zenia solution.

Braman (12) of the Air Force developed an automatic monitoring system that uses the nuclear reaction of beryllium for its detection.

Emission spectroscopy is used to determine beryllium in the ashed and extracted samples from the sampling train at the detection limits of 0.0008 $\mu g/m^3$ for urban samples and 0.00016 $\mu g/m^3$ for nonurban samples (13).

Inductively coupled argon plasma (ICAP) is a recommended EPA detection method for beryllium (14). A detection limit of 0.3 μg/L at 313.0 nm wavelength is reported.

Atomic absorption spectrophotometry (AAS) is the preferred method (15,16,17,18) for analyzing sampling trains. The analysis is performed on the hydrochloric acid solution of the wet-ashed sample using a nitrous oxide/acetylene flame at 234.9 nm wavelength setting. Interferences are controlled by addition of 8-hydroxyquinoline. The detection limit of this method is 0.002 μg/mL and the working range is 0.03-3 μg/mL (4).

DISCUSSION/RECOMMENDATIONS

Method 104 is the recommended method for sampling and analysis of beryllium because it:

- shows to be 100 percent effective in recovering beryllium compounds from stack gases.
- employs the reliable, sensitive, and convenient AAS detection method.
- Allows for detailed studies of the distribution of beryllium compounds in the sampling train.

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SAMPLING AND ANALYSIS PROCEDURES FOR CADMIUM

BACKGROUND

Cadmium is a relatively rare metal that does not occur in nature in the pure form (concentration in earth's crust is 0.000055 percent); however, cadmium occurs mainly in the form of minerals in zinc, lead-zinc, copper-zinc, and lead-copper-zinc ores (1). All ores containing zinc also contain cadmium with a weight ratio of cadmium-to-zinc ranging from 0.0002 to 0.002 (2). The main emission sources of cadmium are metal and metal-related industries. Other emission sources include pesticides and fertilizer manufacturing industries and coal burning facilities (coal typically has 1 gram of cadmium per ton) (3).

Table B-4 is a summary of the physical and chemical properties of cadmium and those of its compounds that may be emitted as air pollution (1).

Cadmium and compounds are recognized as highly toxic materials to biological systems both human and animal. Emissions to air containing cadmium element or compounds when inhaled may produce the following disorders: proteinuria (caused from kidney damage), pulmonary emphysema and bronchitis, osteomalacia (itai-itai disease), and gastric and intestinal disorders. Cadmium iodide, used in the pottery and electroplating industry as a lubricant and in manufacture of phosphorus, and cadmium acetate, when inhaled in the form of dust and fumes, can cause throat dryness, cough, headache, vomiting, chest pain, and irritability. Cadmium chloride, used in photography and vacuum tube and pigment industries, can also cause similar disorders. Cadmium oxide used in the phosphorus, semiconductor, glass, silver alloy, and ceramic industries, when inhaled at a concentration of 2.5 g/m^3 of air for one minute, is fatal (1) while 31 g/m^3 for 1-12 years (4) produced no effects. In a 1964 study (1), the average atmospheric concentration of cadmium was found to be 0.002 g/m^3 with 0.35 μg/m^3 being the maximum value recorded. Cadmium is also suspected as a cause for heart disease (5) and as a carcinogen.

SAMPLING METHODS

Because of the relatively low volatility of cadmium and cadmium compounds, a Method 5 type train equipped with the appropriate particulate collector appears to be the most popular approach for sampling cadmium emissions from stationary sources.

EPA Method 5 as modified effective September 19, 1977 (6) was used to sample particulate matter such as cadmium dust by withdrawing the sample isokinetically into the sampling train. The train consists of the following components: a stainless steel or glass probe nozzle with an appropriate liner (e.g., borosilicate or quartz glass) capable of maintaining a gas temperature at the exit of 120°C ± 14°C; an S type pitot tube; a differential pressure gauge; a borosilicate glass filter holder; a filter heating system capable of maintaining a temperature of 120°C ± 14°C during sampling; and a condenser system consisting of four impingers for determining the stack gas moisture content. The first and second impingers in the condenser system are of the modified (6) Greenberg-Smith design and contain known amounts of water; the third is the same design but empty; and the fourth is the same design but with no modification and is filled with a desiccant (silica gel, calcium sulfate, or any other appropriate material). In addition, the sampling train includes a metering system consisting of a vacuum gauge, leak-

TABLE B-4. PHYSICAL AND CHEMICAL PROPERTIES OF CADMIUM AND SOME CADMIUM COMPOUNDS

Compound	Physical Properties	Chemical Properties
Cadmium metal (Cd)	m.p. 320.9°C b.p. 766.0°C Density - 8.64 g/cm^3 Vapor density 1.36 g/L (766°C) Atomic number 48	Group II element Valency-divalent Oxidation - • powder burns in air with a red flame; vapor reacts with water vapor to form oxide Solubility - • dissolves in mercury (5.9% at 25°C) • displaces copper and other nobler metals from their solutions
Cadmium oxide (CdO)	Sublimes at 1770°K (1 atm)	Solubility - • insoluble in water
Cadmium sulfide (CdS)	Vapor pressure 0.1 mm Hg (765°C) crystal dimension of cubic form—a = 5.82 A°	Solubility - • 1.5×10^{-10} moles/L (H_2O)
Cadmium sulfate ($CdSO_4$)	Density 4.96 g/cm^3 m.p. 1000°C	Solubility - • 76.88 g/100 g water (0°-74.5°C)
Cadmium chloride ($CdCl_2$)	m.p. 568°C b.p. 960°C Density 405 g/cm^3 Crystal dimension (hexagonal—a = 3.85°A, c = 17.46A°) Vapor pressure 23 mm Hg(712°C)	Solubility - • 128.6 g/100 g water
Cadmium acetate $Cd(CH_3COO)_2$	m.p. 255°C (anhydrous)	

free pump, thermometer, volume measuring gas meter, barometer, and gas density determination equipment. The sample is recovered from the system by washing the nozzle and probe liner with acetone and combining the wash eventually with the particulate matter collected on the filter and filter holder.

Peters, *et al.* (7) proposed and tested a sampling train similar to Method 5 type trains for particulate sampling. The system was all glass in order to avoid metal contamination. Stack emissions were isokinetically sampled from the source at an appropriate rate (0.014-0.028 m^3/min) and for sufficient period to collect a 24-hour representative sample (recommended minimum sampling period is 2 hours). The main components in the system were: a stainless steel or glass nozzle with sharp, tapered leading edge; a sheathed borosilicate glass probe with a heating system capable of maintaining a minimum gas temperature in the range of the stack temperature; a pitot type S tube, or equivalent, attached to a probe to monitor stack gas velocity; differential pressure gauge to measure velocity head to within 10 percent of the minimum value; filter holder made of borosilicate glass; impingers (four Greenberg-Smith type); metering system; and a barometer. The first two impingers contained 0.1M nitric acid each, the third impinger was left empty, and the fourth contained 200 g of preweighed silica gel. The filter was a high efficiency Atelman Microquartz fiber filter (99.95 percent efficiency on 0.3 μ dioctyl phthalate smoke particles). Samples containing cadmium were recovered by combining the contents of the first three impingers, acetone, water, and nitric acid probe washes and the filter holder, the filter and the particulate on the filter holder.

Hamersma, *et al.* (8) developed a similar sampling train for high pressure gas sampling for gasifier outputs that included a pressure reduction system, a modified ASTM liquid sampling probe (9), a water condensing impinger and a series of impingers containing 3M H_2O_2 (for removing acid gases), a series of three impingers containing 3M H_2O_2, 0.2M $(NH_4)_2S_2O_8$, and 0.02M $AgNO_3$ for trace metal (cadmium) absorption, and a fourth impinger containing Drierite. This method is applicable for sampling outputs with temperatures of up to 500°C and pressures of no greater than 300 psig under isokinetic sampling conditions. Sampling rate is 2-10 m^3 of gas over 1-4 hour period.

EPA Level 1 Source Assessment Sampling (SASS) train (10) has been by far the most widely used system for sampling inorganics including cadmium and cadmium compounds. This system is mainly designed to collect large quantities of particulate matter, size classified in the range of 10 μ, 3-10 μ, 1-3μ and <1 μ, and inorganic volatile species that can be liquid absorbed. The sampling train consists mainly of a probe, which enters an oven module containing three cyclones and a filter designed to give the particulate delineation from <1—<1-10μ an impinger series containing $(NH_4)_2S_2O_8$, $AgNO_3$, high purity water and H_2O_2, and a high volume vacuum pump. It is designed to operate up to 205°C in flue gas streams, and to operate unattended if the degree of nonisokinetic sampling level varies widely.

Flegal, *et al.* (11,12) designed a system to sample flue gas streams for trace inorganic materials based on a standard Aerotherm high volume stack sampler (HVSS) with the following modifications: (1) the probe was lined with an inner removable liner made of Kapton polyimide film to prevent contamination from stainless steel components, (2) Gelman Spectrograde type A glass fiber filter was used as the filtering medium, and (3) a special oxidative impinger system consisting of four impingers: one impinger with 3M H_2O_2, two impingers with O.2M $(NH_4)_2S_2O_8$ plus 0.2M $AgNO_3$, and a fourth with Drierite. The impinger nozzles are Teflon coated to prevent corrosion of the SS components due to the oxidative solutions. This system is designed to operate in a flue gas stream at temperatures up to 450°C with a sampling rate of up to 90 L/min.

In all the above sampling procedures, sample recovery is accomplished by evaporating the acetone/water washes and combining the residue with the liquid absorbent in the impinger and the nitric acid digest of particulate matter from the filter and filter holder.

ANALYTICAL PROCEDURES

Following is a survey of the most commonly used analytical techniques for determining cadmium at the μg level after a sample has been ashed if it is in the solid form or brought to dissolve in water or mineral acids if in other forms.

Saltzman (13) and Setterlind, *et al.* (14) developed a colorimetric method to determine trace amounts of cadmium spectrophotometrically by using diphenylthiocarbazone (Dithizone) as the complexing agent. This method is applicable to samples containing as much as 5-10 μg of common interfering metals. The separation is improved by the use of cyanide as a suppressing agent in two extractions from a strongly alkaline solution and by the use of tartaric acid as the stripping medium. The detection limit of this method is 0.05 μg in 15 mL sample with 95 percent recovery.

Levine (15) and Ferret, *et al.* (16) determined cadmium concentrations in air using polarography. The sample was ashed and later neutralized. Cadmium was precipitated as cadmium sulfate and determined using a polarographic radiometer. The sensitivity of the method is better than 0.18 g mL in the final solution.

Cadmium analysis in air was also accomplished using emission spectroscopy (ES) (17,18). The samples were ashed or concentrated and extracted (19) prior to determination by ES. The detection limits for cadmium in urban air samples was found to be 0.011 $\mu g/m^3$ and for nonurban samples 0.004 μg/m.

Neutron activation analysis (20) was found to have a detection limit of 0.005 g cadmium in a final solution of $\leq$10 mL (in the absence of interfering species). Unfortunately, the technique is not readily available in standard analytical laboratories because of the need for the prohibitively expensive neutron generator and supporting equipment.

Wagman, *et al.* (21) reported limits of 0.002 g/cm cadmium by X-ray fluorescence. Because of the nondestructive nature of this technique combined with excellent sensitivity and speed of analysis, it provides a reliable approach to cadmium analysis in spite of a high initial investment. With continuous improvements in resolution, sensitivity, and reliability combined with a trend towards reducing costs, this technique is becoming more and more competitive with traditionally less expensive techniques like AAS.

Atomic Absorption Spectrophotometry (AAS) is the most widely used technique for determining cadmium content in sampling train collectors. AAS with flame (22) was found to have a detection limit of 0.005 μg/mL (23) with 0.02-2 μg/mL being the working range. Stanford Research Institute (24) recommends the use of an air/acetylene flame and 228.8 nm wavelength setting in acid solutions obtained from the sampling train. In the event of interferences, cadmium can be extracted into ammonium pyrollidine carbodithioate in methyl isobutylketone (APCD/MIBK) or as cadmium iodide (from 0.1M potassium iodide) into MIBK.

Improvement in sensitivity is obtained by AA/Graphite Furnace (flameless) techniques. A detection limit of 0.1 μg/L with an optimum concentration range of 0.5-10 μg/L is obtained with 96-98 percent recoveries (25).

McKown, *et al.* (26) developed a method for cadmium analysis in solid matrices that have high background noise levels. The method is based on Zeeman Atomic Absorption Spectrophotometry (ZAAS). This technique has the ability to correct for background absorbances as high as 1.7 absorbance units making it possible perhaps to analyze for trace amounts of cadmium in solid adsorbing materials.

EPA (27) reports that inductively coupled argon plasma (ICAP) can be used routinely to determine cadmium in liquid samples with a lower detection limit of 4 μg/L at 226.5 nm wavelength. This technique offers adequate sensitivity and low operational expense if several other metals are to be determined simultaneously.

DISCUSSION/RECOMMENDATIONS

Table B-5 summarizes the advantages and disadvantages of the most commonly used sampling and analysis procedures. Based on this summary the ADL modified Method 5 train (7) is recommended for the determination of cadmium in combustion emissions because this system:

- Collects particulate cadmium containing compounds on appropriate filter (MSA 1106 BH, Gelman Spectrograde (without silicone), ADL/Balston Microquartz, Millipore AA, or Millipore Fluoropore FA).
- Collects volatile cadmium containing species in nitric acid containing impingers which can be analyzed without complicated handling procedures.
- Provides for desired detection limits of cadmium [~5 ppb using AAS (flame) and 0.1 ppb using AAS (flameless)].
- Is flexible and can be easily modified.
- Allows for using different detection techniques in cases where unexpected interferences occur.

TABLE B-5. ADVANTAGES AND DISADVANTAGES OF CADMIUM SAMPLING AND ANALYSIS PROCEDURES

Procedure	Advantages	Disadvantages
EPA Method 5 train	Simple train, sufficient for collecting cadmium in particulate form Combination with AAS provides specificity and speed analysis Available commercially	Does not collect volatile components efficiently Not adequate for low levels because of small sample size Cannot be used without modification Impinger system not designed for metal collection
EPA SASS train	Effective in collecting volatile and nonvolatile cadmium compounds (good filter and impinger systems) Provides sensitivity by allowing for large sample collection Combination in the AAS provides desired sensitivity and reliability	Complex and expensive train Difficult to clean Stainless steel parts corrode when exposed to acidic fumes Difficult to modify
ADL Method 5 train (7)	Combines benefits of Method 5 and SASS Sampling rate and sample size can be determined accurately Has an adequate impinger system for collecting cadmium and its compounds Provides heating system to prevent condensation of sample in wrong locations	Not available commercially More complex to operate than SASS Does not contain an oxidizing liquid in the impinger system for general oxidation of possible interfering species
High pressure	Effective for sampling high pressure stalks because of a well designed pressure reduction system Same as SASS	Same as for SASS Special application

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SAMPLING AND ANALYSIS PROCEDURE FOR NICKEL

BACKGROUND

Nickel is present at about 0.016 percent in the earth's crust. It is a greyish-white, hard, tough, and resistant to oxidation and corrosion. Nickel minerals are most commonly sulfides, oxides, silicates, and arsenicals (1). The properties of nickel and some nickel compounds are listed in Table B-6.

TABLE B-6. PROPERTIES AND TOXICITY OF NICKEL AND SOME NICKEL COMPOUNDS(1)

Compound	Properties	Toxicity
Nickel Ni	Lustrous white, hard, ferromagnetic metal m.p. 1453°C b.p. 2839°C Soluble in dilute HNO_3 Density 8.90 g/cm^3 (25°C)	May cause dermatitis in sensitive individuals. Ingestion of soluble salts causes nausea, vomiting, diarrhea
Nickel acetate $Ni\,(C_2H_3O_2)_2 \cdot 4H_2O$	Green crystalline mass or powder b.p. 16.6°C Density 1.744 g/cm^3	
Nickel arsenate $Ni_3(AsO_4)_2 \cdot 8H_2O$	Yellowish-green powder Density 4.982 g/cm^3 Insoluble in water	
Nickel bromide $NiBr_2 3H_2O$	Yellowish-green very deliquescent crystals m.p. 963°C	
Nickel carbonate hydroxide $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	Green, odorless powder	

TABLE B-6. (Continued)

Compound	Properties	Toxicity
Nickel carbonyl $Ni(CO)_4$	Yellow volatile liquid m.p. -25°C bp 43°C Decomposes at 60°C Insoluble in water Soluble in most organic solvents Density 1.32 g/cm^3 (25°C) Vapor Pressure 400 mm (25°C)	Poisonous! Vapors may cause irritation, congestion, and edema of lungs. Prolonged exposure may cause cancer of lungs, nasal sinuses. Odor threshold 1-3 ppm
Nickel chloride $NiCl_2 \cdot 6H_2O$	Green, deliquescent crystals or powder Sublimes at 973°C	LD iv in dogs 10,000 to 20,000 μg/kg
Nickel cyanide $Ni(CN)_2 \cdot 4H_2O$	Apple green powder Insoluble in water	Poisonous!
Nickel dimethylglyoxime $C_8H_{14}N_4NiO_4$	Scarlet-red crystalline powder Sublimes at 250°C	
Nickel fluoride NiF_2	Yellow to green tetragonal crystals Sublimes in HF stream above 1000°C	Chronic exposure may cause mottling of teeth changes in bones. See Nickel
Nickel hydroxide $Ni(OH)_2 \cdot H_2O$	Apple-green powder, ignited in air at about 400°. Insoluble in water	
Nickel monoxide NiO	Green powder Insoluble in water m.p. 1990°C	
Nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$	Green, deliquescent crystals m.p. 56.7°C b.p. 137°C	
Nickel oxalate $NiC_2O_4 \cdot 2H_2O$	Light green powder Insoluble in water	
Nickel phosphate $Ni_3(PO_4)_2 \cdot 7H_2O$	Light green powder Insoluble in water	

TABLE B-6. (Continued)

Compound	Properties	Toxicity
Nickel potassium sulfate $K_2Ni(SO_4)_2 \cdot 6H_2O$	Bluish-green crystals Soluble in water	
Nickel sesquioxide Ni_2O_3	Gray-black powder Decomposes 600°C	
Nickel sulfate $NiSO_4 \cdot 6H_2O$	Emerald-green transparent crystals, sweet astringent taste	L.D.s.c. in guinea pigs 62 μg/g
Dicyclopentadienyl-nickel $(C_5H_5)Ni$	Sublimes at 130°C Soluble in alcohol	
bis (Cyclopentadienyl-nickel carbonyl) $(C_5H_5NiCO)_2$	m.p. 136°C	
Dicyclopentadiene-nickel $(C_5H_6)_2Ni$	m.p. 41-42°C	

The most common sources of nickel emissions are metallurgical plants using nickel, engine burning fuels containing nickel additives, burning coal and oil, nickel plating facilities, and incineration of nickel products. In 1964, concentration of nickel in urban air averaged 0.032 $\mu g/m^3$ and ranged up to a maximum of 0.69 $\mu g/m^3$ (2). Nickel emissions from stationary sources are mainly particulate in nature except for the volatile nickel carbonyl and some organic complexes used as fuel additives.

SAMPLING METHODS

Trace amounts of nickel can be determined using a sampling train developed by Hamersma, *et al.* (3,4). This system is designed to sample high pressure outputs under isokinetic conditions. The sampling train consists of a modified ASTM liquid sampling probe, an impinger for condensing liquid water and oils in an ice bath under pressure, followed by pressure reduction and a second impinger series. The second set of impingers where nickel and its compounds are expected to be found consists of Impinger No. 1 containing 3M H_2O_2, Impinger Nos. 2 and 3 containing 3M H_2O, 0.2M $(NH_4)_2\ S_2O_8$ and 0.02M $AgNO_3$, and

Impinger No. 4 containing Drierite for drying the sampling gases. The sampling train is applicable to outputs with temperatures up to 500°C and pressures greater than 300 psig. Sampling rates of 2 to 10 m^3 of gas over 1- to 4-hour period with detection limits of 60 $\mu g/m^3$ of the volatile trace element in the gas stream.

A similar system for normal pressure flue gas sampling for trace inorganic materials was designed by Flegal, *et al.* (3,5). The sampling train consists of a standard Aerotherm high volume stack samples (HVSS) modified in three areas: (1) the probe was lined with an inner removable liner made of Kapton polyimide film to prevent nickel, chromium, and other stainless steel elements from contaminating the particulate catch; (2) Gelman Spectrograde type A glass fiber filter was used as the filtering medium, and (3) a special oxidative impinger system was developed to sample vaporous elements and their compounds. The oxidative system consists of four impingers: one impinger with 3M H_2O_2, two impingers with 0.2M $(NH_4)_2 S_2O_8$ plus 0.02M $AgNO_3$, and a fourth impinger with Drierite. The impinger nozzles are coated with Teflon to prevent corrosion of the stainless steel components due to the oxidative solutions. The system is designed to operate in a flue gas stream at temperatures up to 270°C and sampling rate of up to 90 L/m (3 cfm).

EPA Method 5 as modified effective September 19, 1977 (6) was used to sample particulate matter such as nickel dust by withdrawing it isokinetically into the sampling train. The train consists of the following components: a stainless steel or glass probe nozzle with an appropriate liner (e.g., borosilicate or quartz glass) capable of maintaining a gas temperature at the exit of 120°C ± 14°C; an S type pitot tube; a differential pressure gauge; a borosilicate glass filter holder; a filter heating system capable of maintaining a temperature of 120°C ± 14°C during sampling; and a condenser system consisting of four impingers for determining the stack gas moisture content. The first and second impingers in the condenser system are of the modified Greenberg-Smith design and contain known amounts of water; the third is the same design but empty; and the fourth is the same design but with no modification and is filled with a desiccant (silica gel, calcium sulfate, or any other appropriate material). The system also includes a metering system consisting of a vacuum gauge, leak-free pump, thermometer, volume measuring gas meter, barometer, and gas density determination equipment. The sample is recovered from the system by washing the nozzle and probe liner with acetone and combining the wash eventually with the particulate matter collected on the filter and filter holder.

Peters, *et al.* (7) proposed and tested a sampling train similar to Method 5 type trains for particulate sampling. The system was all glass in order to avoid metal contamination. Stack emissions were isokinetically sampled from the source at an appropriate rate (0.014-0.028 m^3/min) and for sufficient period to collect a 24-hour representative sample (recommended minimum sampling period is 2 hours). The main components in the system were a stainless steel or glass nozzle with sharp, tapered leading edge, a sheathed borosilicate glass probe with a heating system capable of maintaining a minimum gas temperature in the range of the stack temperature, a type S pitot tube, or equivalent, attached to a probe to monitor stack gas velocity, differential pressure gage to measure velocity head to within 10 percent of the minimum value, filter holder made of borosilicate glass, impingers (four Greenberg-Smith type), metering system, and a barometer. The first two impingers contained 0.1M nitric acid each, the third impinger was left empty, and the fourth contained 200 g of preweighed silica gel. The filter was a high efficiency Gelman Microquartz fiber filter (99.95 percent efficiency on 0.3 diotyl phthalate smoke particles).

EPA Level 1 Source Assessment Sampling (SASS) train (8) has been the most widely used system for sampling inorganics, including nickel and compounds. This system is mainly designed to collect large quantities of particulate matter, size classified in the range of 10 μ, 3-10 μ, 1-3 μ and <1 μ as well as inorganic volatile species that can be liquid absorbed. The sampling train consists mainly of a probe, which enters an oven module containing three cyclones and a filter designed to give the particulate delineation from <1-10 μ, an impinger system containing $(NH_4)_2\ S_2O_8$, $AgNO_3$, high purity water and H_2O_2, and a high volume vacuum pump. It is designed to operate up to 205°C in flue gas streams, and to operate unattended if the degree of nonisokinetic sampling level varies widely.

A high-volume filtration sampler (9) used by the National Air Sampling Network was found to be applicable for particulate sampling only and ignores volatile compounds like nickel carbonyl.

ANALYTICAL PROCEDURES

Nickel can be detected colorimetrically using dimethylglyoxime as the complexing agent (10). West, *et al.* (11) adapted the ring-oven technique for the determination of nickel particulates using dimethylglyoxime as the complexing agent. Neutron activation analysis (NAA) was used (12) to determine nickel levels at the microgram level; however, the detection limit of 0.7 μg makes this technique not as attractive as atomic absorption spectrophotometry (AAS) or X-ray fluorescence spectrometry (XRF). X-ray fluorescence spectrometry (XRF) (13) is a fast and reasonably sensitive technique for nickel analysis. The detection limit is 0.01 $\mu g/cm^3$. Flame Emission Spectrophotometry (FES) is capable of detecting 0.03 μg/mL nickel in solution (14).

Atomic absorption spectrophotometry (AAS) is by far the most popular technique for measuring nickel in solution. The reported detection limit is 0.005 μg/mL (14), and the linear range for accurate measurement is reported as 0.2-5 μg/mL when 232.0 nm wavelength setting and an oxidizing air/acetylene flame are used (15). In a 10 mL sample, the mass range for accurate measurement is 2.50 μg. AAS analysis is especially appropriate for nickel because there are no known interferences. However, a hundredfold excess of iron, manganese, chromium, copper, cobalt or zinc may decrease the absorbance recorded for nickel by as much as 12 percent (16). Proper burner elevation and use of an oxidizing flame can minimize this effect. High solids content in the aspirated solution will cause increased nonspecific absorbance at the 232 nm line setting (16). Thompson *et al.* (17) reported that the National Air Pollution Control Administration found that the minimum detection limit for nickel by AAS is 0.004 $\mu g/m^3$ based on a 2,000 m^3 air sample.

Inductively coupled argon plasma (ICAP) has gained prominence recently as a fast and reliable analytical tool for nickel determination when multielement analysis is required (18). The detection limit using the 231.6 nm line is 15 μg/L (19). Due to the high toxicity and common occurrence of nickel carbonyl in industrial emissions, specific analytical methods were developed for monitoring (1).

Brief, *et al.* (20) described the following methods for the determination of nickel carbonyl:

(1) An air sample can be assured through a saturated solution of sulfur in trifluoroethylene. The sulfur reacts with nickel to form a precipitate. Spectrographic examination is sensitive to 0.0003 ppm nickel carbonyl.

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(2) An air sample may be drawn through a tube containing red mercuric oxide at 200°C, and the liberated mercury may be determined spectrographically. A parallel stream of air is drawn through an oxidizing reagent to convert the CO to CO_2, and the stream is passed over mercuric oxide; the liberated mercury is again determined spectrographically. The difference in the amounts of mercury vapor measured corresponds to the nickel carbonyl content in the air. A sensitivity of 0.0014 ppm is reported.

(3) Nickel carbonyl may be absorbed in chloramine. The nickel determination is accomplished colorimetrically using dimethylglyoxime. For a 30-minute sample, at the suggested sampling rate of 0.5 liter per minute, a sensitivity of 0.01 ppm is obtained.

(4) Another colorimetric method uses iodine in carbon tetrachloride as the collection medium. The nickel is colored with dimethylglyoxime. A sensitivity of 0.1 ppm to nickel carbonyl is claimed.

(5) Nickel carbonyl may be collected in dilute sulfuric acid followed by spectrophotometry using sodium diethyl-dithiocarbamate as the coloring agent.

(6) A sample was collected by Brief, *et al.* (20) in dilute hydrochloric acid in a midget impinger (0.1 cfm for 30 minutes). The nickel was complexed with alpha-furildioxime and extracted with chloroform. The nickel content is determined spectrophotometrically. The method is sensitive to 0.0008 ppm.

A field method described by Kobayashi (21) appears to be appropriate for analysis of nickel carbonyl in a sampling train. The sample is drawn through a tube filled with silica gel impregnated with 0.5 percent gold chloride. In the presence of nickel carbonyl, the silica gel changes from a light yellow to bluish-violet. The concentration of nickel carbonyl is a function of the length of the colored layer. The useful range of a 100-mL sample is 200 to 600 ppm. By measuring the minimum volume of test gas needed to color the silica gel at a constant sampling rate, the concentration of nickel carbonyl to 3 ppm can be determined.

In another method (22), the test air is drawn at 0.5 L/min through an absorption tube containing two 15-mm-diameter filter papers and then through two absorption vessels with porous plates. Each plate contains 3 mL of 1.5 percent solution of chloramine-B in alcohol. The chloramine-B solution retains the nickel carbonyl vapor. The colored vapor is compared with standards. The sensitivity of the method is 1 g of nickel carbonyl; the error does not exceed 10 percent.

DISCUSSION/RECOMMENDATIONS

The ADL modified EPA Method 5 (7) combined with atomic absorption with flame is the recommended approach because:

- The sampling train is capable of collecting both the volatile and nonvolatile nickel compounds.
- Based on nine replicate experiments the precision of the nickel measurement is 11.4 percent and the accuracy 3.9 percent at about 100 μg level.
- The quartz filter used is effective in trapping nickel particulate.

- The impinger system (0.1M HNO_3) is appropriate for nickel sampling and allows for modification without additional cost if special trapping solutions are to be used for organometallic components.
- AAS detection method is interference free and accurate for nickel analysis using air/acetylene and the 232.0 nm line.

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APPENDIX C

SAMPLING AND ANALYSIS PROCEDURES FOR ASBESTOS

SAMPLING AND ANALYSIS PROCEDURES FOR ASBESTOS

BACKGROUND

Airborne asbestos has been successfully sampled and analyzed from many environments, but it has never been sampled in the discharge from a combustion furnace. Thus a research effort is needed to establish the required methodology. First, one must realize that the fuel probably will not contribute asbestos (as explained in Section 4 on emissions) to the atmosphere, but asbestos may originate due to contamination by insulation used in the construction of the furnace.

Second, one must be aware that the presence of airborne ash will make the detection of asbestos fibers very difficult. This creates a problem of finding a few very small asbestos fibers among a large number of much larger fly ash particles. Indeed, the stability of the asbestos minerals makes asbestos a suitable construction material for joint sealing and insulation of combustion furnaces.

Asbestos is a generic term for a variety of hydrated silicate minerals which have one common attribute, namely, the ability to be separated into relatively soft, silky fibers. Although the name is ordinarily associated with those varieties that have technologic importance, it is applicable to all minerals that fit the above description. The term "asbestiform minerals" is perhaps most descriptive.

The known varieties of asbestiform minerals can be divided into two main classes on the basis of their crystal structures: serpentine and amphiboles. The sole member of the serpentine class is chrysotile asbestos, which is by far the most common of the asbestiform minerals. It accounts for more than 95 percent of the asbestos fiber produced today. Crocidolite, amosite, tremolite, actinolite, and anthophyllite are the amphibole varieties.

The commercial deposits of "asbestos" contain one of the following minerals:

chrysotile, $Mg_3Si_2O_5(OH)_4$;

amosite, $(Fe^{2+}2Mg)_7Si_8O_{22}(OH)_2$ (a variety of grunerite);

crocidolite, $Na_2(Fe^{2+},Mg)_3Fe_2{}^{3+}Si_8O_{22}(OH)_2$ (a variety of riebeckite);

"fibrous" anthophyllite, $(Mg,Fe)_7Si_8O_{22}(OH)_2$; and

"fibrous" tremolite and actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$.

Tremolite and actinolite are of little economic importance; anthophyllite is of little economic importance now.

The physical and chemical properties of the asbestiform minerals can be directly related to their crystal structure and chemical composition. In turn, the physical and chemical properties are responsible for the commercial importance of asbestos. It is understandable, therefore, that great emphasis has been placed on the elucidation of the structure and composition of these important minerals.

The airborne asbestos which may be found emanating from the insulating construction components of a combustion furnace will be difficult to observe and identify because of the small number of nanometer sized asbestos fibers dispersed among a large number of micrometer sized ash particles. This configuration can probably best be dealt with by employing a separation procedure prior to analysis by transmission electron microscopy (TEM). The status of airborne asbestos analysis is typified by the work of Samudra, *et al.* (1) which led to the publication of a provisional methodology manual (2). This work recognized that the use of polycarbonate filters in the field presented handling problems and that the cellulose ester filter would be a more suitable field sampling medium. Since methods for direct transfer of cellulose ester filter deposits to electron microscope grids have been shown to be unreliable (3), a modified technique is required by which representative and reproducible proportions of the cellulose ester filter deposit can be transferred to an electron microscope grid.

Although preparation of polycarbonate filters for the microscope is simple and direct by the carbon-coating procedure, in practice the properties of this filter make it a most unsuitable medium for field use. In addition to the extreme difficulty of handling this thin filter in the field, experience has shown that particulate material becomes detached during transportation and handling. The material is either lost or at least moved to other parts of the filter surface. It is then impossible to subsample this filter in a representative manner. The direct preparation technique associated with the Nucleopore filter also has no particular advantage if the filter is overloaded, as is often the case with environmental samples. The alternative is to sacrifice some of the analytical simplicity in favor of a filter which is more satisfactory for field use. The sponge structure of the conventional membrane filter retains the particulate in position during normal handling and transportation. The collection of air samples for electron microscopy differs from water sampling in that the analyst usually does not have control over the filter loading. To obtain a correctly loaded filter for direct examination implies a foreknowledge of the source particulate loading, the variable under investigation. It is possible to operate several samplers simultaneously using different air flows or for a range of sampling times. Unfortunately, neither of these alternatives yields the same information from the sample since source concentrations are rarely constant over a sufficiently long period. There is no reason why samples averaged over different periods of time should give the same result, and operation of air samplers at different values of airflow generates different flow patterns and consequently results in variations of sampling characteristics.

A simple solution to this problem is to collect the sample on the cellulose ester filter and then to transfer it quantitatively to a polycarbonate filter. Since the direct transfer techniques for preparation of cellulose ester filters as electron microscope samples have been shown to be unreliable, the only alternative direct transfer technique available is that reported by Ortiz and Isom (4), known as the collapsing Millipore technique. In this method, the cellulose ester filter with the deposit on its surface is exposed to acetone vapor resulting in collapse of the sponge texture into a continuous plastic film. The particulates retained on the surface of this plastic film can then be transferred quantitatively to the electron microscope by the carbon-coating procedure with dissolution similar to that of the polycarbonate approach. Unfortunately, using large pore size Millipore filters causes many fibers to penetrate the structure and become engulfed during the collapsing procedure. These fibers do not transfer to the final replica. However, this technique has not been sufficiently evaluated and it is possible that use of a small pore size Millipore for air sampling may give an adequate recovery. However, as pore sizes become smaller, the sample movement problems associated with the Nuclepore filter also become more serious for the Millipore filter.

It is generally agreed that in air sampling work, the 0.8 μm pore size cellulose ester filter has a collection efficiency for airborne particulate in excess of 99 percent. However, this collection efficiency has not been established for small chrysotile fibrils. Work by Spurny, *et al.* (5) demonstrates graphically the reasons for improved surface retention of particulate on the Millipore filter. Fibers can be speared perpendicularly into the surface structure. There is indeed some evidence that many fibers approach the filter surface oriented in the direction of flow; where this occurs, chrysotile fibrils would be capable of penetrating even the 0.1 m pore size Nuclepore filter. The extent to which this occurs will depend on the relative importance of the sieving, impaction, and direct interception filtration mechanisms. Marchio, *et al.* (6) carried out some studies of the filtration efficiences for asbestos fibers using Nuclepore filters. These studies showed that a Nuclepore filter with pore diameter of 0.8 μm has a mean efficiency of about 80 percent for sampling chrysotile fibrils. Spurny, *et al.* have performed efficiency measurements for Nuclepore filters of different pore sizes using neutron activated amosite. The filtration efficiences ranged from 75 percent for a 8 μm pore size to 97.4 percent with 0.6 μm pore size. For ambient air sampling, they recommend the use of Nuclepore filters with a pore size of 0.4 μm and estimate their mean efficiency for atmospheric fibers as high as 95 percent. In another study, Gentry and Spurny (7) have shown collection efficiencies of 50-90 percent, using amosite aerosols collected on Nuclepore filters of different pore sizes. The data also show that using the 0.8 μm pore size Nuclepore filter, the collection efficiency does not appear to vary as a function of face velocity in the range of 3-24 cm/sec. Electron micrographs shown in this study indicated that the fibers were able to penetrate Nuclepore filters with pores less than 20 percent of the fiber length.

Fiber bundles pose a problem during analysis in the TEM. One must make a decision whether to merely note the presence of a fiber bundle or to attempt to count and measure the fibers within the bundle. Frequently, the fiber bundle represents a major quantity of the asbestos found in a TEM preparation. The best approach to dealing with fiber bundles needs to be identified.

There is need for a standardized sampling method, improved sample preparation, and analytical procedures for electron microscopy. The EPA Provisional Method represents a considerable improvement and should be adopted until a better method is provided.

SAMPLE COLLECTION AND HANDLING

Determining the airborne number or mass concentration of any aerosol requires a procedure that entails several sequential steps, each of which can influence the determination. For example, the sample can be affected by the geometry and mode of operation of the sampler, by the filter medium, by the transportation mode of the loaded filter between field and laboratory, and by the technique employed to assess the loading. A recent in-depth study for the EPA (1) looked at some of the influences and isolated a subset of these requiring further research.

There are significant contaminants in combustion furnace atmospheres, often components of coatings on fibers. For example, those originating from asbestos cement pipe manufacture are often coated with cement particles, an effect which makes identification of the fibers difficult. Chatfield, *et al.* (3) found that no effects on chrysotile fibers can be found as a consequence of limited exposure of the fibers to dilute hydrochloric acid. Exposures of thirty minutes or more to 20 percent HCl at room temperature were shown to produce no detectable effects. The work of Stasnney, *et al.* (8) also demonstrated that limited exposure to dilute nitric acid does not significantly affect the fiber. It would appear that the incorporation of an acid extraction step would improve the sensitivity of the analytical technique, remove some of the interfering contaminants which may be attached to fibers, and not involve any additional steps in the analytical procedure. However, the effect on the uniformity and dispersal of the fibers on the final prepration have not yet been investigated. It is suggested that suitable aqueous dispersal media would be water, dilute aerosol OT, sodium pyrosulfate solution, and both dilute hydrochloric and nitric acids.

At this time, the filter stage of a Method 5 sampler or SASS train is believed to be suitable for arresting the asbestos containing materials from coal- and fuel-oil fired stationary sources. It should be pointed out that use of these samplers for collecting asbestos requires validation since the authors are not aware of any careful studies employing these sampling trains.

QUANTITATIVE IDENTIFICATION OF ASBESTOS MINERALS BY EDXA

Several authors have concluded that the unequivocal identification of asbestos fibers using EDXA alone is not possible. However, in many cases the identification of individual fibers by means of elemental analysis is sufficient from the practical point of view. Attempts to do this have so far been strictly qualitative in approach and have usually involved the computation of peak areas for magnesium, aluminum, silicon, calcium, and iron from the X-ray emission spectrum of the fiber. Peak areas of all the other elements are referred to that for silicon and the resulting peak area ratios are compared with those obtained from suitable standards. Unfortunately, the peak area ratios are not constant as the fiber diameter changes. The extent of this variation is a function of the composition of the fiber. Moreover, since each individual species of asbestos has a variable composition, even from fiber to fiber, and often along the length of an individual fiber, determination of an exact composition may not be sufficiently specific for a precise identification to be made. Attempts to obtain accurate chemical composition data in the TEM by EDXA are compromised by both sample and instrumental artifacts. In the TEM, there are a number of spurious sources of X-radiation which are seen by the X-ray detector and contribute to the spectrum obtained. Such spurious sources include parts of the specimen holder in the vicinity of the beam, the sample support mesh itself and other components in the electron optical column which are sufficiently close to the beam to be excited by stray electrons. As for the sample itself, any large particles in close proximity to the particle being irradiated will also contribute to the spectrum and this must be taken into account.

Some preliminary work in discrimination between the amphibole asbestoses using only EDXA spectra has been conducted by Millette (9). In this work the "Discriminate Analysis" statistical procedure was employed to classify the amphiboles. The input to this calculation consisted of the peak areas of sodium, magnesium, silicon, calcium, and iron referred to the peak area of silicon; background subtraction and fiber dimension corrections were not made. Discrimination of the asbestos minerals from other species, and in particular discrimination between the amphibole types themselves, will be more specific if quantitative measurements are made. It is proposed to use the peak to background method reported by Small *et al.* (10) and Statham and Pawley (11) in which the peak intensities for the elements in the particle are related to ZAF corrected bulk sample peak intensities. In this way, compositional analyses would be obtained which are corrected for the particle size effect and thus reduce the spread of data due to this cause. This technique would be combined with the step-wise discriminant technique initially applied to the problem by Millette (9). In all of this proposed method, samples would be mounted on gold grids to avoid interference with the NaK line by the CaKα line of copper.

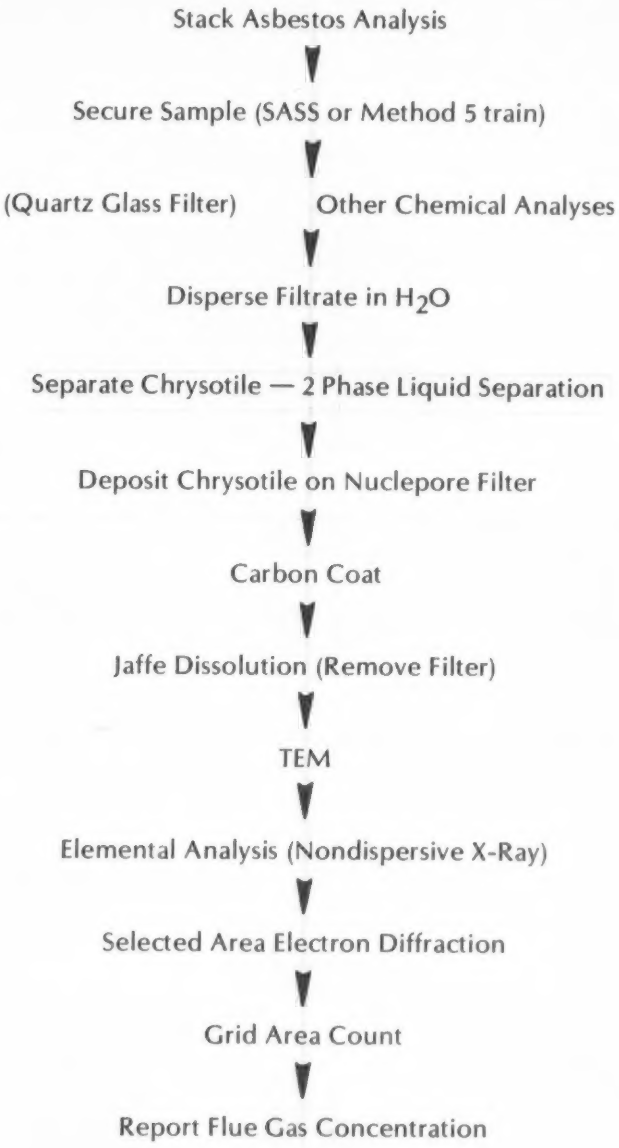
DISCUSSION/RECOMMENDATIONS

Illinois Institute of Technology (IIT) (12) is currently conducting a program for EPA to determine optimum sampling conditions for airborne asbestos.

In the interim it would appear that stack sampling for asbestos presents as least two special problems: (1) the use of a sampling system which can operate at stack temperatures, and (2) the separation of asbestos fibers from all other material found in the furnace emissions. The problem of sampling at stack temperatures means that the filter should be glass or quartz fiber (another source of fibers). Both the SASS train and Method 5 train can use either glass or quartz fiber filters for particulate collection and thus are satisfactory from that point of view. The EPA Method 5 specifies glass fiber filters which have a 99.5 percent collection efficiency of 0.3 μm dioctyl phthalate (DOP) smoke particles. The EPA Level 2 method recommends either high efficiency glass fiber filters (Reeve Angel 934AH) or quartz fiber filters (Gelman Micro Quartz) for operation of the SASS train.

For Level 2 SASS sampling the filter holder is generally maintained at 195-200°C and the volume of gas sampled yields at least 100 mg of total particulate. A sample of flue gas particulate material collected in this manner could be divided for asbestos analysis and other required chemical analyses. A representative blank filter would be included to determine background fiber interferences.

The problem of separation of the background material can be solved for chrysotile fibers by dispersing the filtrate in water and then using the two-phase separation developed by Melton (13). Chrysotile has a positive zeta potential which makes it possible to separate it from other materials by the two-phase liquid separation. All of the amphibole asbestos fibers have a negative zeta potential and do not separate by using the two-phase liquid separation. Following is an outline which may be used for asbestos analysis of stack samples:



Stack Asbestos Analysis

Secure Sample (SASS or Method 5 train)

(Quartz Glass Filter) Other Chemical Analyses

Disperse Filtrate in H_2O

Separate Chrysotile — 2 Phase Liquid Separation

Deposit Chrysotile on Nuclepore Filter

Carbon Coat

Jaffe Dissolution (Remove Filter)

TEM

Elemental Analysis (Nondispersive X-Ray)

Selected Area Electron Diffraction

Grid Area Count

Report Flue Gas Concentration

SUMMARY OF ASBESTOS PROCEDURE

- No precedent for sampling and analysis of stack emissions for asbestos has been established.
- Impinger of cyclone sample collection may work as well as filtration.
- Sampling by filtration presents some filter problems at stack temperatures.
- Separation of asbestos from ash material is necessary.
- Type of analysis depends upon the size of the asbestos fibers.
- Fibers smaller than 1 μm will need to be analyzed by TEM.
- Fibers larger than 1 μm can be analyzed by light microscopy.
- The following diagram, Figure C-1, shows a simplified schematic of the general asbestos scheme, but does not indicate a specific procedure for separating asbestiforms from other particulate species.

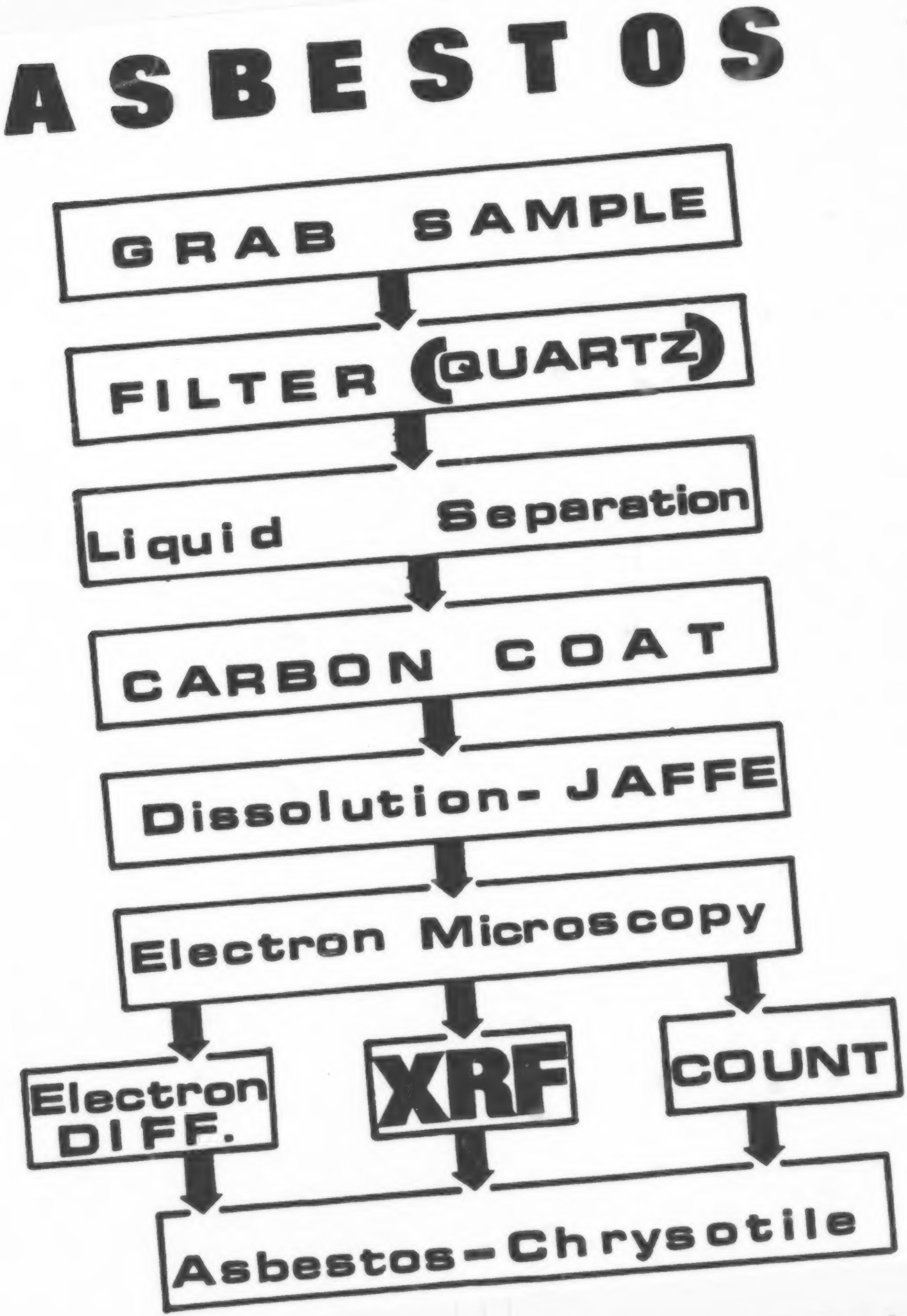

ASBESTOS
GRAB SAMPLE
FILTER (QUARTZ)
Liquid Separation
CARBON COAT
Dissolution- JAFFE
Electron Microscopy
Electron DIFF.
XRF
COUNT
Asbestos-Chrysotile

Figure C-1. Schematic diagram of analysis method for asbestos in stack samples.

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